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Volume II. Appendices

Radian Corp, Austin, Tex.

Prepared for

Industrial Environmental Research Lab, Research Triangle Park, N C

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EXPERIMENTAL AND THEORETICAL STUDIES OF SOLID SOLUTION FORMATION IN LIME AND LIMESTONE SO_2 SCRUBBERS

VOLUME II. APPENDICES

by

Benjamin F. Jones, Philip S. Lowell, and Frank B. Meserole

Radian Corporation
8500 Shoal Creek Boulevard
Austin, Texas 78766

Contract 68-02-1883
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EPA Project Officer: Robert H. Borgwardt

Industrial Environmental Research Laboratory
Office of Energy, Minerals, and Industry
Research Triangle Park, NC 27711

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VOLUME II

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16. ABSTRACT

The report gives results of a theoretical and experimental study to characterize the coprecipitation of calcium sulfate with calcium sulfite hemihydrate. A coprecipitation product had been suggested to explain the mechanism by which sulfate could be precipitated from a scrubber solution subsaturated with respect to calcium sulfate. Lime and limestone SO2 scrubbing systems with oxidation rates below 20% had been operated long-term at steady state with liquors subsaturated with respect to all known calcium sulfate solid forms and yet sulfate was measured in the solids. The existence of a calcium sulfate/calcium sulfite solid solution has been confirmed experimentally and a theoretical formulation has been established. Calcium sulfite hemihydrate was precipitated under controlled laboratory conditions from solutions subsaturated in calcium sulfate. Specific chemical analysis and infrared spectroscopic techniques were used to identify sulfate in the solids. The precipitate's sulfate content was studied as a function of the relative saturation of calcium sulfate and the precipitation rate of calcium sulfite hemihydrate. Also, the effects of high magnesium concentrations and limestone dissolution on the sulfate content of the solids were measured.

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Calcium Oxides	Stationary Sources	07B
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APPENDIX A

"THERMODYNAMICS OF THE SOLID SOLUTION SERIES $(CaSO_3/CaSO_4)\cdot\frac{1}{2}H_2O$"

Prepared by:
Philip S. Lowell

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1.0 INTRODUCTION

The Environmental Protection Agency has done a considerable amount of work that indicates that sulfate can be removed from aqueous solution as a "coprecipitate" of calcium sulfite. Borgwardt and co-workers (BO-143, BO-144, OP-012, OP-014) have established that this phenomenon depends on solution composition, precipitation rate, and other variables.

Radian is under contract to EPA to help explain and quantify this phenomenon. A first step is to determine if the coprecipitation is predominantly an equilibrium or a kinetics effect. Because the driving force for many rate processes is a difference between actual and equilibrium conditions, a description of the equilibrium phenomenon will be of value no matter what the predominant effect (kinetics or equilibrium) is.

In Section 2.0 a relationship between aqueous and solid phase calcium sulfite and sulfate will be developed. Then in Section 3.0 a means of quantifying the relationship from experimental data will be given.

2.0 THEORY

Components in two different phases are in equilibrium when the chemical potentials in both phases are equal. The problem then, is to relate the chemical potentials in the aqueous and solid phases.

The chemical potential of a component "i" in a phase "j" may be defined in terms of an activity, a_{ij}, and a standard state potential, μ°_{ij}.

$$\mu_{ij} = \mu^{\circ}_{ij} + RT \ln a_{ij} \tag{2-1}$$

For convenience we define:

$i = 1 \Rightarrow CaSO_3 \cdot \frac{1}{2}H_2O$
$i = 2 \Rightarrow CaSO_4 \cdot \frac{1}{2}H_2O$

$j = s \Rightarrow$ Solid
$j = \ell \Rightarrow$ Liquid

For the solid we will define the standard state as the pure component. For a solid solution mixture we will consider deviations from ideal solutions based on mole fraction. Solid phase activity coefficients are defined by Equation 2-2.

$$a_{1s} = \sigma_1 x_1 \tag{2-2a}$$

$$a_{2s} = \sigma_2 x_2 \tag{2-2b}$$

The activities of $CaSO_3$ and $CaSO_4$ in the liquid phase are defined in Equation 2-3.

$$a_{1\ell} = a_{Ca^{++}} a_{SO_3^=} a_w^{\frac{1}{2}} \qquad (2\text{-}3a)$$

$$a_{2\ell} = a_{Ca^{++}} a_{SO_4^=} a_w^{\frac{1}{2}} \qquad (2\text{-}3b)$$

The liquid phase is in equilibrium with the solid phase when the chemical potentials are equal. Equating chemical potentials gives Equation 2-4.

$$\mu_{is} = \mu_{i\ell} \qquad (2\text{-}4)$$

Substituting in the definitions in Equations 2-1, 2-2, and 2-3 into 2-4 gives Equation 2-5.

$$\mu^\circ_{is} + RT\ \ell n\ \sigma_i x_i = \mu^\circ_{i\ell} + RT\ \ell n\ a_{i\ell} \qquad (2\text{-}5)$$

Equation 2-5 may be solved for the activities.

$$\frac{a_{i\ell}}{\sigma_i x_i} = e^{-(\mu_{i\ell} - \mu_{is})/RT} \qquad (2\text{-}6a)$$

$$= K_i \qquad (2\text{-}6b)$$

The equilibrium constant, K_i, turns out to be the solubility product constant. This may be seen by taking the limit of pure components, i.e., $\sigma_i x_i \rightarrow 1$. The relationship between solid and liquid at equilibrium for the species is written out in explicit form.

$$a_{Ca^{++}} a_{SO_3^=} a_w^{\frac{1}{2}} = K_1 \sigma_{CaSO_3} x_{CaSO_3} \qquad (2\text{-}7a)$$

$$a_{Ca^{++}} a_{SO_4^=} a_w^{\frac{1}{2}} = K_2 \sigma_{CaSO_4} x_{CaSO_4} \qquad (2\text{-}7b)$$

The coprecipitation of sulfate is thermodynamically stable so long as there is no other mechanism that will cause an even greater decrease in system free energy. One such point is the transition from solid solution in sulfite to pure hemihydrate sulfate. This occurs at the point given in Equation 2-8.

$$a_2 s = 1 < \sigma_2 x_2 \qquad (2\text{-}8)$$

A second limit would be the formation of gypsum. The solubility product of gypsum is given in Equation 2-9.

$$\mathrm{CaSO_4 \cdot 2H_2O}_{(s)} \rightarrow \mathrm{Ca^{++}} + \mathrm{SO_4^{=}} + \mathrm{2H_2O} \qquad (2\text{-}9a)$$

$$K_3 = \frac{a_{\mathrm{Ca^{++}}} a_{\mathrm{SO_4^{=}}} a_w^2}{a_{\mathrm{CaSO_4 \cdot 2H_2O}_{(s)}}} \qquad (2\text{-}9b)$$

The sulfate transition from solid solution hemihydrate to gypsum is given in Equation 2-10.

$$\mathrm{CaSO_4 \cdot \tfrac{1}{2}H_2O}_{(s)} + \tfrac{3}{2}\mathrm{H_2O} \rightarrow \mathrm{CaSO_4 \cdot 2H_2O}_{(s)} \qquad (2\text{-}10)$$

The criterion for this transition to take place is Equation 2-11.

$$1 < \frac{K_2}{K_3} \sigma_2 x_2 a_w^{3/2} \qquad (2\text{-}11)$$

3.0 COMPUTATIONAL PROCEDURES

The only unknowns at present are solid phase activity coefficients. What is required is a plot of solid phase activity coefficients as a function of solid phase composition. This is shown schematically in Figure 3-1. Liquid and solid phase composition data are required for the aqueous and solid phases in equilibrium.

Our task is to relate chemical potential in the liquid phase to chemical potential in the solid phase. Activities may be used to relate chemical potentials through Equations 2-1 or 2-6.

Liquid phase activities may be calculated from known phase compositions in a routine fashion using the Radian Aqueous Ionic Equilibrium (AIE) program. The thermodynamic constants relating liquid phase activities to solid phase activities (solubility product constants) are also known.

The solid phase activity coefficients, the σ_i's of Equation 2-6b or 2-7 are not known at this time. These must be calculated from liquid phase compositions in equilibrium with solid phase compositions at a known temperature.

$$\sigma_i = \frac{a_{i\ell}}{K_i x_i} \qquad (3\text{-}1)$$

Since the activity coefficient data will be obtained at constant temperature and pressure, they may be checked for thermodynamic consistency using a modified form of the Gibbs-Duhem equation as shown in Equation 3-2.

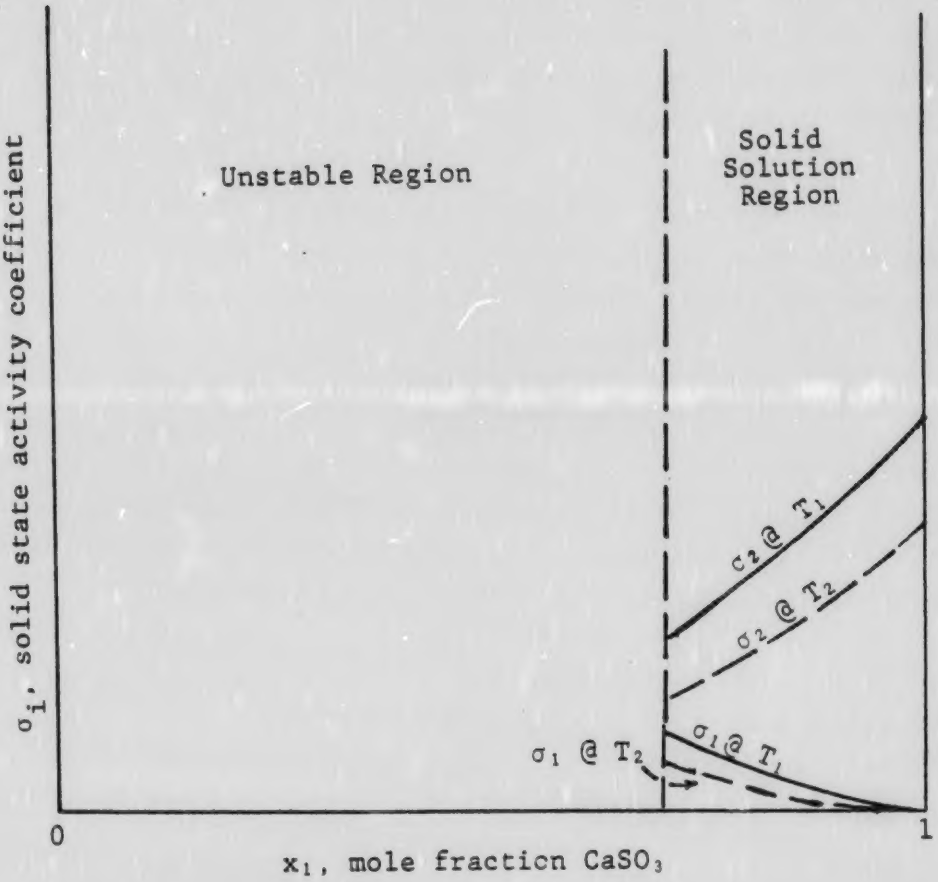

FIGURE 3-1 - SCHEMATIC SOLID STATE ACTIVITY COEFFICIENT

$$x_1 \frac{\partial \ell n \sigma_1}{\partial x_1} = -x_2 \frac{\partial \ell n \sigma_2}{\partial x_1} \qquad (3\text{-}2)$$

The procedure for calculating and correlating solid phase activity coefficients will be as follows.

- The liquid phase composition will be input to the Radian AIE program. The activities of Ca^{++}, $SO_3^{=}$, $SO_4^{=}$, and H_2O will be calculated.
- Liquid phase activities for $CaSO_3$ and $CaSO_4$ will be calculated from Equation 2-3.
- From the above and the solid phase composition the solid phase activity coefficient will be calculated for one composition with Equation 3-1.
- A series of different solid-liquid equilibria points will be calculated, plotted as in Figure 3-1, and the thermodynamic consistency checked with Equation 3-2.

REFERENCES

BO-143 Borgwardt, R. H., *Limestone Scrubbing of SO_2 at EPA/RTP Pilot Plant*, Progress Report 21, Research Triangle Park, N.C., EPA, June 1975.

BO-144 Borgwardt, R. H., *Sulfate Scale Control in Lime/ Limestone Scrubbers by Unsaturated Operation*, Draft Report, Research Triangle Park, N.C., EPA, May 1974.

OP-012 Opferkuch, R. E., *Limestone Scrubbing of SO_2 at EPA Pilot Plant*, Progress Report 10, Research Triangle Park, N.C., EPA, p. 6, May 1973.

OP-014 Opferkuch, R. E., *Limestone Scrubbing of SO_2 at EPA Pilot Plant*, Progress Report 11, pp. 6-9, Research Triangle Park, N.C., EPA, June 1973.

APPENDIX B

"A REVIEW OF PLANT AND PILOT PLANT DATA RELATING TO THE FORMATION OF THE SOLID SOLUTION SERIES $(CaSO_3/CaSO_4)\cdot\frac{1}{2}H_2O$"

Prepared by:
Jay R. Hoover

Reviewed by:
W. E. Corbett

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1.0 INTRODUCTION

Radian is under contract to EPA to perform a theoretical and experimental study of the factors which control the coprecipitation of calcium sulfate with calcium sulfite in lime/limestone SO_2 scrubbing systems. As part of an early phase of this program, pilot plant and full scale system performance data relating to the coprecipitation phenomenon which were available to EPA were reviewed by Radian. The purpose of this data review was twofold:

- to define ranges of operating conditions under which coprecipitation is observed to occur. This information is important because it defines the variables to be considered in the experimental phases of the program which follow.
- to provide a basis for comparing the results obtained in Radian laboratory experiments with "real" system performance.

In this technical note, results of Radian's data review subtask are reported. Soluble component activities which were calculated using Radian's aqueous ionic equilibrium program are reported for those cases where sufficient data were given. Calculated precipitation rates based upon EPA pilot unit data are also presented.

All of the data which were reviewed by Radian as part of this effort were supplied by EPA. These data came from four major sources.

The Environmental Protection Agency has obtained a considerable amount of data on calcium sulfite/sulfate coprecipitation in lime and limestone wet scrubbing systems in pilot plant studies conducted at Research Triangle Park, North Carolina. In addition, data supplied to EPA by Imperial Chemical Industries (ICI) on their Bankside power plant, by Arthur D. Little, Inc. (ADL) in the report "Scale Control in Limestone Wet Scrubbing Systems", and by Louisville Gas and Electric (LG&E) on their Paddys Run scrubber were made available to Radian. Also, considerable data from the TVA-Shawnee facility were supplied to Radian by Bechtel Corporation.

2.0 METHODS OF DATA ANALYSIS

The types of information which are considered to be potentially important for purposes of characterizing calcium sulfate/sulfite coprecipitation in lime/limestone SO_2 scrubbing systems are listed below:

- liquid phase compositions and pH,
- liquid phase activities,
- driving forces for precipitation (relative saturations),
- precipitation rates of calcium sulfite and sulfate,
- solid phase compositions.

Liquid phase activities and relative saturations were calculated using the Radian aqueous ionic equilibrium program for all data points for which the composition and pH of the hold tank liquor were known. Precipitation rates were also calculated whenever possible.

The ICI and ADL data transmitted to us were incomplete as far as this program was concerned since no liquor compositions or hold tank data were reported. Complete liquid and solid phase analyses for a significant fraction of the LG&E test runs were also not available. For this reason, almost all of the meaningful test data considered here are based upon EPA/RTP pilot plant studies. Only the three complete LG&E data points are reported. Sources of these data are listed in the Reference Section. An example of a typical EPA data reporting sheet is shown in Figure 1.

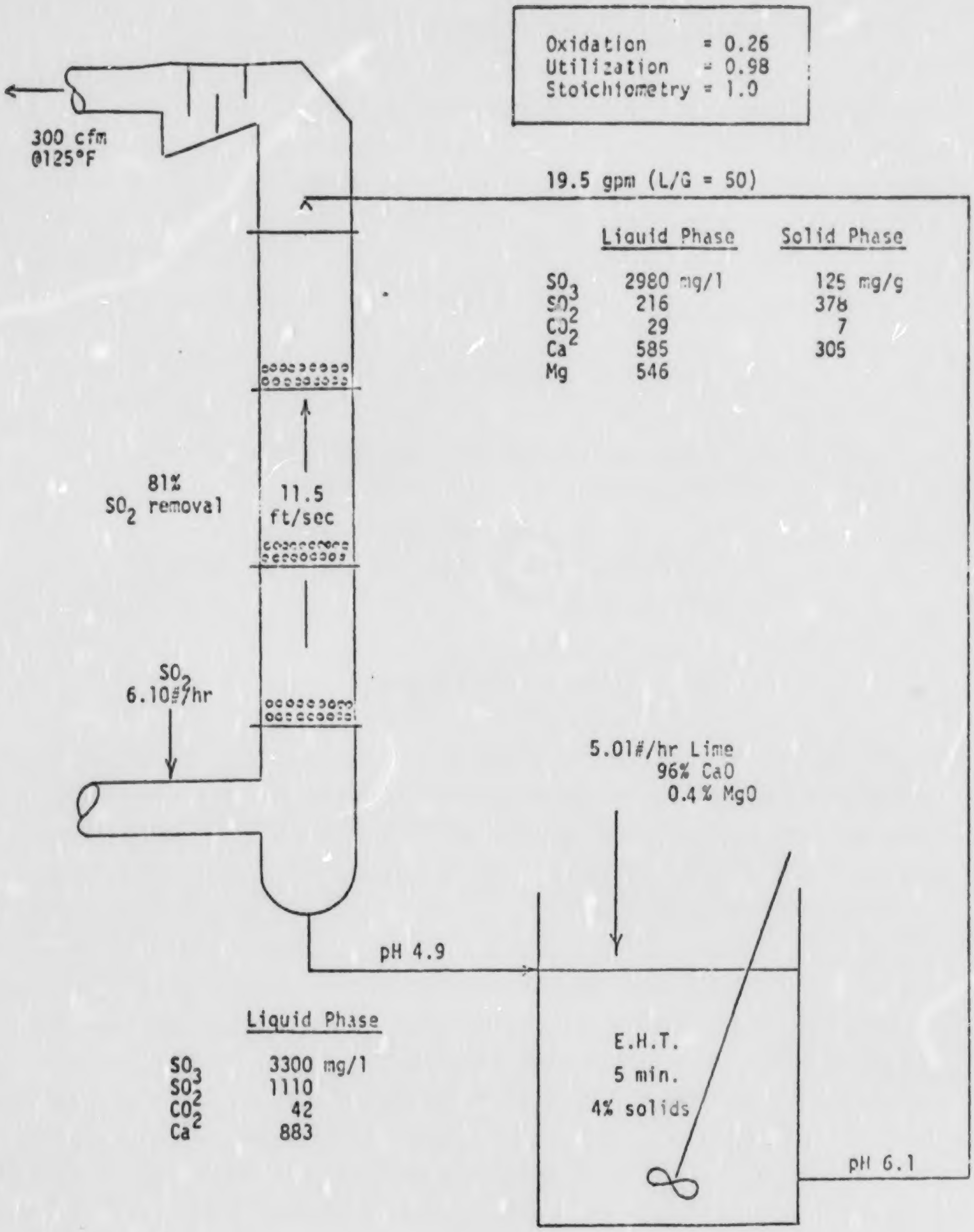
Oxidation = 0.26
Utilization = 0.98
Stoichiometry = 1.0
300 cfm
@125°F
19.5 gpm (L/G = 50)
Liquid Phase
Solid Phase
SO_3 2980 mg/l 125 mg/g
SO_2 216 378
CO_2 29 7
Ca 585 305
Mg 546
81%
SO_2 removal
11.5
ft/sec
SO_2
6.10#/hr
5.01#/hr Lime
96% CaO
0.4 % MgO
pH 4.9
E.H.T.
5 min.
4% solids
pH 6.1
Liquid Phase
SO_3 3300 mg/l
SO_2 1110
CO_2 42
Ca 883

FIGURE 1 - TYPICAL EPA PILOT UNIT DATA REPORT SHEET

An indication of some of the problems involved in analyzing the EPA and LG&E results can be gained by considering the simplified schematic representation of an SO_2 scrubbing process shown in Figure 2. In this figure, the significant vessels, i.e., scrubber and hold tank, and the phenomena which take place in each are identified.

SO_2 sorption is the primary function of the scrubber. Sulfite oxidation can occur in both the scrubber and the hold tank. Sulfite precipitation (and sulfate coprecipitation) takes place in the hold tank.

As SO_2 is sorbed, the pH of the scrubber liquor and the relative saturation of $CaSO_3$ tend to drop. Under these conditions, some dissolution of $CaSO_3$ solids would be expected.

Obviously the relative rates at which these various reactions proceed are extremely complex functions of the operating variables and process configurations involved in each case. Finding a meaningful basis for the separation of these various effects was the key problem which was faced in the analysis of the data.

Some of the equations which can be written to describe the steady state performance of the system shown in Figure 2 are discussed below.

For the Overall System

$$\begin{aligned} & SO_2 \text{ Sorption Rate} \times (1 - OX) \\ & \quad = \text{Sulfite Solids Removal (or Accumulation) Rate} \end{aligned} \tag{2-1}$$

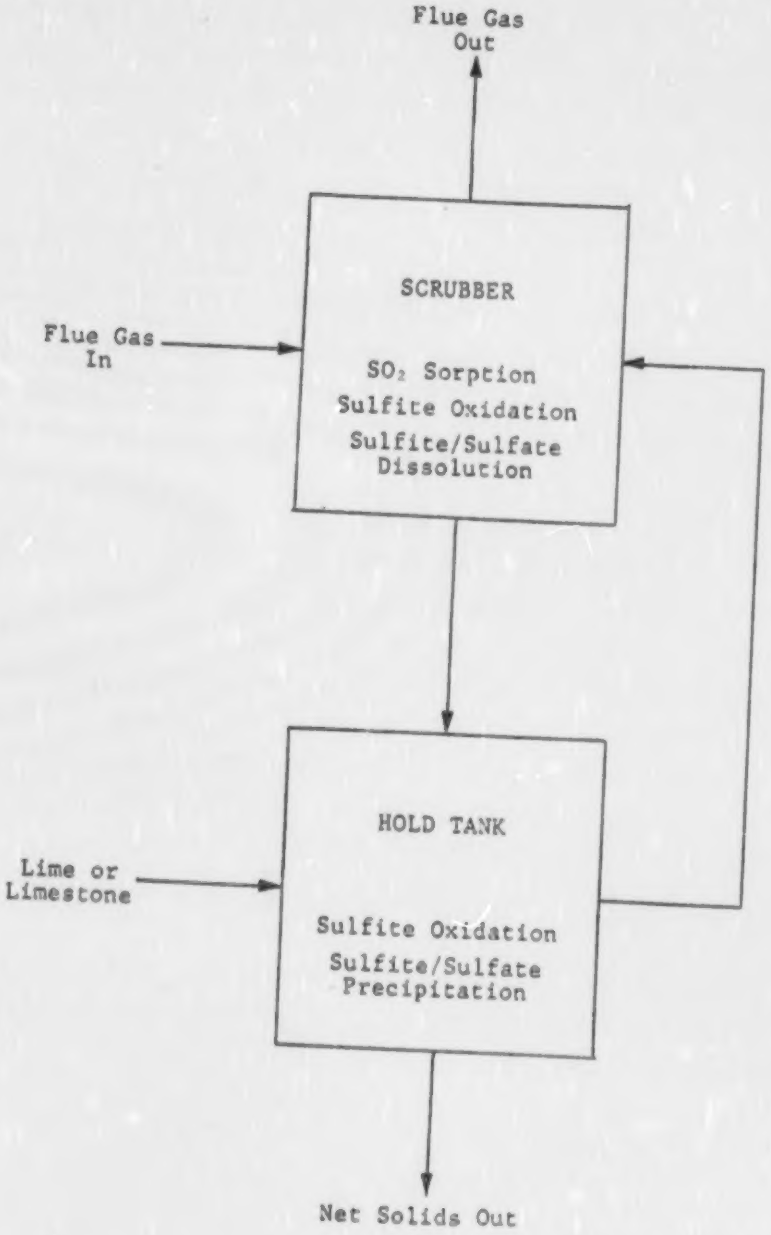
Flue Gas Out
SCRUBBER
Flue Gas In
SO₂ Sorption
Sulfite Oxidation
Sulfite/Sulfate Dissolution
HOLD TANK
Lime or Limestone
Sulfite Oxidation
Sulfite/Sulfate Precipitation
Net Solids Out

FIGURE 2 - SIMPLIFIED SCHEMATIC VIEW OF TYPICAL SO_2 SCRUBBING PROCESS

$$\mathrm{SO_2\ Sorption\ Rate} \times \mathrm{OX} = \text{Sulfate Solids Removal (or Accumulation) Rate} \qquad (2\text{-}2)$$

where OX is the fraction of the incoming sulfur in the +4 oxidation state (SO_2 or $SO_3^=$) which is ultimately oxidized and removed from the system as sulfur in the +6 oxidation state ($SO_4^=$). Physically, OX is defined by Equation 2-3.

$$\mathrm{OX} = \frac{\text{Sulfite Oxidation Rate in Scrubber} + \text{Sulfite Oxidation Rate in Hold Tank}}{\mathrm{SO_2}\ \text{Sorption Rate}} \qquad (2\text{-}3)$$

however, OX can also be accurately approximated as

$$\mathrm{OX} = \frac{\text{Sulfate in Net Solids Out}}{\text{Total Sulfur } (SO_3^= + SO_4^=) \text{ in Net Solids Out}} \qquad (2\text{-}4)$$

For the Circulating Sorbent Liquor

$$\begin{aligned} \mathrm{SO_2}\ \text{Sorption Rate} &= \text{Sulfite Oxidation Rate (Scrubber + Hold Tank)} \\ &\quad + \text{Sulfite Precipitation Rate (Scrubber + Hold Tank)} \end{aligned} \qquad (2\text{-}5)$$

$$\begin{aligned} &\text{Sulfite Precipitation Rate (Scrubber + Hold Tank)} \\ &\quad = \text{Sulfite Solids Removal (or Accumulation) Rate} \end{aligned} \qquad (2\text{-}6)$$

Sulfite Oxidation Rate (Scrubber + Hold Tank)

= Sulfate Precipitation Rate (Scrubber + Hold Tank)

= Sulfate Solids Removal (or Accumulation) Rate (2-7)

As these equations are written, sulfite/sulfate dissolution in the scrubber is treated as a negative precipitation term.

An additional equation which can be written to describe the performance of the hold tank is

Hold Tank Sulfite In (Liquid Phase)
- Hold Tank Sulfite Out (Liquid Phase)

= Sulfite Precipitation Rate (Hold Tank)
+ Sulfite Oxidation Rate (Hold Tank) (2-8)

It follows from Equation 2-8 that when the sulfite oxidation rate is zero (sealed hold tank runs), the sulfite precipitation rate in the hold tank can be calculated as

Sulfite Precipitation Rate (gmoles/min)

= [Liquid Phase Sulfite In (gmoles/ℓ)
- Liquid Phase Sulfite Out (gmoles/ℓ)]

× Liquid Flow Rate (ℓ/min) (2-9)

An equivalent expression can be used to calculate sulfate precipitation rates for sealed hold tank runs.

If the sulfite oxidation rate in the hold tank is significant and unknown, the direct computation of sulfite precipitation rates from hold tank data is impossible. Sulfite and sulfate precipitation rates cannot be calculated from solid phase analyses because the quantity of solids precipitated in the hold tank is small compared to the quantity of seed crystals present.

As a result of these considerations, hold tank precipitation rates were not calculated for unsealed hold tank runs or for runs in which inlet and outlet hold tank liquor compositions were not given. In some such cases, net sulfite precipitation rates were calculated from Equations 2-1 and 2-6. This term was determined only because it was not possible to calculate gross precipitation rates (hold tank only). Obviously, gross precipitation rates would be more appropriate for purposes of determining whether a correlation exists between $SO_3^=$ precipitation rates and solid phase sulfite/sulfate ratios. Depending on the relative significance of the scrubber solids dissolution rate term, the net precipitation rates calculated using this approach may or may not be a good approximation of true gross hold tank precipitation rates.

The LG&E data were given for runs in which an unsealed hold tank was used. However, the surface area to volume ratio was so small (due to the 220,000 gallon capacity) that the hold tank oxidation rate was assumed negligible and these data were treated in the same fashion as the EPA sealed hold tank results.

In addressing the influence of kinetics on solids composition it is necessary to normalize the data to a meaningful consistent basis. This was done by calculating precipitation rates on the basis of moles precipitated/min/gram seed. The procedures used to normalize the precipitation rates calculated by the procedures described above will now be discussed.

In the case of the EPA test results, the amounts of calcium sulfite and sulfate seed were calculated from reported $CaCO_3$ slurry densities and $CaCO_3$-to-$CaSO_3$ molar ratios using Equations 2-10 and 2-11.

$$\text{Sulfite Seed}\left(\frac{\text{g } CaSO_3\cdot\frac{1}{2}H_2O}{\ell}\right) =$$

$$\left(\frac{129\text{ g } CaSO_3\cdot\frac{1}{2}H_2O}{\text{gmole } CaSO_3\cdot\frac{1}{2}H_2O}\right)\left(\begin{array}{c}\text{Mole Ratio of}\\ CaSO_3 \text{ to } CaCO_3\end{array}\right)\left(\frac{\text{gmole } CaCO_3}{100\text{ g } CaCO_3}\right)\left(\begin{array}{c}\text{g } CaCO_3/\ell\\ \text{in Slurry}\end{array}\right) \qquad (2\text{-}10)$$

$$\text{Sulfate Seed}\left(\frac{\text{g } CaSO_4\cdot\frac{1}{2}H_2O}{\ell}\right) =$$

$$\text{Sulfite Seed}\left(\frac{OX}{1-OX}\right)\left(\frac{145\text{ g/mole } CaSO_4\cdot\frac{1}{2}H_2O}{129\text{ g/mole } CaSO_3\cdot\frac{1}{2}H_2O}\right) \qquad (2\text{-}11)$$

These quantities were then used to normalize the calculated precipitation rates to units of (gmole/min)/g total seed ($CaSO_3$ + $CaSO_4$).

LG&E seed concentrations were calculated directly from solid phase analyses as shown in Equations 2-12 and 2-13.

$$\text{Sulfite Seed}\left(\frac{\text{g } CaSO_3\cdot\frac{1}{2}H_2O}{\ell}\right) =$$

$$\left(\frac{\text{gmole } SO_3^{=}(SO_2)}{\text{g Solids}}\right)\left(\frac{129\text{ g } CaSO_3\cdot\frac{1}{2}H_2O}{\text{gmole } SO_3^{=}}\right)\left(\frac{0.1\text{ g Solids}}{\text{g Slurry}}\right)\left(\frac{1100\text{ g Slurry}}{\ell}\right) \qquad (2\text{-}12)$$

↑ 10% Solids Assumed ↓

↑ Slurry Specific Gravity = 1.1 (Assumed) ↓

$$\text{Sulfate Seed}\left(\frac{\text{g } CaSO_4\cdot\frac{1}{2}H_2O}{\ell}\right) =$$

$$\left(\frac{\text{gmole } SO_4^{=}(SO_3)}{\text{g Solids}}\right)\left(\frac{145\text{ g } CaSO_4\cdot\frac{1}{2}H_2O}{\text{gmole } SO_4^{=}}\right)\left(\frac{0.1\text{ g Solids}}{\text{g Slurry}}\right)\left(\frac{1100\text{ g Slurry}}{\ell}\right) \qquad (2\text{-}13)$$

3.0 RESULTS

The EPA and LG&E field data which were considered in this subtask are reported in Tables 3-1 and 3-2. Table 3-1 summarizes unsealed hold tank data and includes pH, liquid composition data, and solid composition data. Table 3-2 presents sealed hold tank data which include not only pH, liquid and solid concentrations, but also precipitation rates. Precipitation rates were determined by the methods discussed in Section 2.0.

Sealed hold tank data were further analyzed at Radian by inputting pH and liquid phase composition into Radian's aqueous ionic equilibrium program. Ionic strength, solution activities, and relative saturations of major species were computed. Activities for calcium, magnesium, chloride, carbonate, sulfite and sulfate are presented in Table 3-3. Relative saturation of calcium sulfite hemihydrate, calcium sulfate hemihydrate, and calcium sulfate dihydrate are also reported. The mole fraction of sulfite and sulfate in the solid phase have also been calculated based on the solid concentration of sulfite and sulfate.

Considerable experimental data from EPA's alkali scrubbing test facility located at TVA's Shawnee Power Station in Paducah, Kentucky, have also been examined. These data covered testing between June 1975 and January 1976 with their venturi/spray tower lime scrubber and their total contact absorber-limestone scrubber. These data, as supplied by Bechtel, include liquid and solid composition data, ionic strength, and relative saturation of calcium sulfate dihydrate. The raw data are not presented but will be graphically presented in Section 4.0. EPA/RTP data will also be analyzed and discussed in Section 4.0.

TABLE 3-1

REPORTED UNSEALED HOLD TANK DATA FROM EPA/RTP PILOT UNIT STUDIES

			Hold Tank Liquid Composition (gmole/ℓ)						Solids Composition (gmole/g)			
Run Date	Feed	pH	Ca	Mg	Cl	CO_3	SO_3	SO_4	Ca	CO_3	SO_3	SO_4
1973:												
Oct 29-Nov 1	LS	5.8	0.0335	0.036	0.088	0.0028	0.0032	0.0226	0.0074	0.0022	0.0031	0.0019
Oct 8-11	LS	5.7	.034	.021	.056	.0041	.0043	.0194	.0061	.0022	.0028	.0008
Nov 13-15	LS	5.7	.034	.031	.071	.0047	.0057	.0248	.0077	.0029	.0034	.0013
Nov 19-21	LS	5.6	.034	.035	.074	.0024	.0078	.00271	.0074	.0017	.0023	.0031
Nov 27-30	LS	5.9	.036	.030	.08	.0036	.0053	.00263	.0077	.0021	.0035	.0016
Dec 3-7	LS	5.9	.037	.029	.072	.0028	.0081	.0216	.0051	.0014	.0024	.0009
Sept 6-11	LS	6.1	.0146	.023	NR	.0007	.0034	.0373	.0076	.0002	.0059	.0016
Sept 11-14	LS	7.1	.0143	.042	NR	.0006	.0029	.0545	.0076	.0003	.0059	.0015
Sept 17-21	LS	8.2	.0167	.018	NR	.0002	.0014	.0314	.0076	.0008	.0056	.0015
Sept 24-28	LS	9.3	.0211	.002	NR	.0006	.0010	.0204	.0076	.0008	.0054	.0013
Oct 1-5	LS	10.2	.0224	.0005	NR	.0002	.0005	.0186	.0076	.0008	.0053	.0008
1974:												
Mar 4-8	LS	6.0	.037	.0625	.188	NR	.0034	.0245	.0079	.0029	.0037	.0012
Mar 18-22	LS	5.8	.033	.0917	.194	NR	.0078	.0463	.0077	.0022	.0025	.0022
Mar 25-29	LS	5.9	.019	.10	.191	NR	.0078	.0438	.0076	.0026	.0039	.0014
Apr 22-26	LS	5.5	.006	.325	.177	NR	.0375	.200	.0074	.0030	.0039	.0014
Apr 1-5	LS	5.6	.014	.238	.226	NR	.0188	.1188	.0077	.0034	.0026	.0019
May 6-10	LS	6.0	.0125	.392	.171	NR	.0313	.250	.0076	.0038	.0038	.0016
May 13-17	LS	5.7	.0093	.696	.397	NR	.144	.374	.0072	.0022	.0033	.0019
May 20-24	LS	5.8	.0108	.563	.240	NR	.103	.350	.0071	.0017	.0034	.0020
May 28-31	LS	5.3	.0055	.308	.120	NR	.042	.139	.0076	.0029	.0041	.0006
June 3-7	LS	5.1	.0195	.304	.22	NR	.013	.188	.0078	.0026	.0039	.0012
June 10-14	LS	5.3	.02	.246	.237	NR	.0155	.131	.0078	.0028	.0041	.0009
1972:												
Aug 22-23	LS	6.4	.0153	NR	NR	.0064	.0026	.033	NR	NR	NR	NR
Sept 12-22	LS	6.3	.016	.035	NR	.0082	.0033	.043	NR	NR	NR	NR
Oct 2-6	LS	6.4	.018	.019	NR	.0036	.0025	.036	NR	NR	NR	NR
Nov 27-29	LS	6.2	.016	.033	NR	.0061	.005	.042	NR	NR	NR	NR
Nov 30-Dec 5	LS	6.3	.0155	.036	NR	.0066	.0041	.045	NR	NR	NR	NR
Apr 19-27	LS	6.1	.0118	.022	NR	.0059	.0066	.025	NR	NR	NR	NR
Apr 30-May 4	LS	6.4	.0084	NR	NR	.0059	.0062	.019	NR	NR	NR	NR
Nov 6-10	LS	6.6	.0155	.0197	NR	.0043	.0025	.039	NR	NR	NR	NR
Nov 14-16	LS	6.6	.0158	.0278	NR	.0036	.0029	.041	NR	NR	NR	NR
Nov 17-22	LS	6.4	.016	.030	NR	.0036	.0036	.041	NR	NR	NR	NR
1973:												
Apr 19-27	LS	6.3	0.012	NR	NR	0.0059	0.0065	0.024	0.0078	0.0016	0.0053	0.0011
May 2-4	LS	6.4	.0084	NR	NR	.0059	.0062	.019	.0079	.0021	.0053	.0011
May 8-10	LS	6.5	.0028	NR	NR	.0086	.0075	.013	.0080	.0017	.0056	.0008
May 14-Jun 6	LS	6.2	.0082	NR	NR	.0059	.0073	.024	.0080	.0022	.0052	.0007
Jun 7-22	LS	5.8	.015	NR	NR	.0056	.0121	.035	.0079	.0028	.0044	.0012
Jul 23-Aug 1	LS	6.3	.0194	NR	NR	.0022	.0027	.021	.0049	.0015	.0021	.0015
Jun 21-22	LS	5.9	.011	0.040	NR	.0051	.0121	.030	NR	NR	NR	NR
Jun 25-29	LS	5.8	.0023	.041	NR	.0058	.0133	.027	NR	NR	NR	NR
July 2-6	LS	6.3	.005	.028	NR	.0068	.0082	.026	NR	NR	NR	NR
July 17-20	LS	6.2	.0024	.022	NR	.0076	.0123	.0155	NR	NR	NR	NR
Apr 29-May 3	L	7.3	.133	.0021	0.237	NR	.0008	.0083	.0053	.0004	.0038	.0008
May 6-10	L	7.0	.085	.0125	.16	NR	.0035	.0063	.0052	.0006	.0044	.0004
May 13-17	L	7.3	.155	.0125	.291	NR	.0011	.0084	.0074	.0004	.0058	.0011
May 20-24	L	7.5	.22	.0083	.42	NR	.0008	.0085	.0075	.0004	.0058	.0007
May 28-31	L	7.1	.165	.0083	.311	NR	.0008	.0121	.0074	.0003	.0055	.0013

TABLE 3-2

REPORTED SEALED HOLD TANK DATA - EPA/RTP AND LG&E TEST RESULTS

Run Date	Feed	pH	Sulfite PPT Rate* (gmole/gm-min) $\times 10^6$	Sulfate PPT Rate* (gmole/gm-min) $\times 10^6$	Hold Tank Liquid Composition (gmole/ℓ)						Solid Composition (gmole/gm)			
					Ca	Mg	Cl	CO_2	SO_2	SO_3	Ca	CO_2	SO_2	SO_3
EPA/RTP DATA 1973:														
Jan 18	LS	6.3	10.14	18.02	0.0158	0.0332	-----	0.00350	0.00540	0.0470	NR	NR	NR	NR
Jan 19	LS	6.2	2.27	1.64	.0165	.0252	-----	.00489	.00552	.0414	NR	NR	NR	NR
Jan 23	LS	6.3	12.56	5.64	.0163	.0325	-----	.00409	.00469	.0512	NR	NR	NR	NR
Feb 5-10	LS	6.3	10.95	4.03	.0169	.0300	-----	.00652	.00409	.0414	NR	NR	NR	NR
Feb 13-22	LS	6.4	20.24	5.08	.0156	.0199	-----	.00650	.00352	.0344	NR	NR	NR	NR
Mar 5-7	LS	6.4	6.33	1.87	.0165	.0089	-----	.00768	.00241	.0195	NR	NR	NR	NR
Mar 12-13	LS	6.6	9.03	.62	.0078	.0081	-----	.00645	.00245	.0090	NR	NR	NR	NR
Mar 14-15	LS	6.6	9.09	2.57	.0096	.0119	-----	.00584	.00245	.0129	NR	NR	NR	NR
Mar 29-Apr 4	LS	6.5	20.96	5.56	.0134	.0137	-----	.00536	.00303	.0199	NR	NR	NR	NR
Apr 9-11	LS	6.6	23.86	3.85	.0119	.0163	-----	.00611	.00348	.0201	NR	NR	NR	NR
May 14-Jun 6	LS	6.2	35.01	4.33	.0082	.0289	-----	.00591	.00730	.0239	NR	NR	NR	NR
Jun 25-29	LS	5.8	22.55	2.78	.0023	.0403	-----	.00577	.01330	.0270	NR	NR	NR	NR
July 2-6	LS	6.3	47.54	10.78	.0081	.0272	-----	.00680	.00823	.0276	NR	NR	NR	NR
July 17-20	LS	6.2	21.96	2.21	.0024	.0214	-----	.00761	.01290	.0155	NR	NR	NR	NR
1974:														
Jan 28-Feb 1	LS	5.6	(15.66)	(2.75)	.0315	.0263	0.056	NR	.0078	.0222	NR	NR	NR	NR
Feb 4-8	LS	5.2	(17.16)	(3.78)	.0218	.1070	.056	NR	.0141	.0475	NR	NR	NR	NR
Feb 11-14	LS	5.9	(17.32)	(3.06)	.0068	.1070	.056	NR	.0109	.0475	NR	NR	NR	NR
Feb 14-15	LS	6.1	(28.30)	(2.14)	.010	.140	.056	NR	.0125	.0775	NR	NR	NR	NR
Feb 19-22	LS	5.9	(26.67)	(2.65)	.015	.165	.155	NR	.0172	.106	NR	NR	NR	NR
Feb 25-Mar 1	LS	5.9	(26.25)	(3.91)	.0375	.078	.177	NR	.0047	.0325	NR	NR	NR	NR
1973:														
Oct 16-19	L	6.0	64.56	9.61	.0156	.0054	.0076	.0006	.0017	.0204	0.0076	0.00034	0.0061	0.00089
Oct 19-23	L	6.7	77.32	13.67	.0108	.0235	.0096	.0008	.00395	.0291	.0075	.00039	.006	.00104
Oct 29-Nov 2	L	7.0	30.13	3.42	.0053	.0473	.0130	.0011	.00567	.0408	.0075	.00029	.0065	.0008

TABLE 3-2 - REPORTED SEALED HOLD TANK DATA - EPA/RTP AND LG&E TEST RESULTS (cont.)

Run Date	Feed	pH	Sulfite PPT Rate* (gmole/gm-min) ×10^6	Sulfate PPT Rate* (gmole/gm-min) ×10^6	Hold Tank Liquid Composition (mole/ℓ)						Solid Composition (gmole/gm)			
					Ca	Mg	Cl	CO_2	SO_2	SO_3	Ca	CO_2	SO_2	SO_3
1973 (cont.)														
Nov 5-8	L	7.3	77.30	25.82	0.0141	0.0405	0.0087	0.0007	0.00367	0.045	0.0075	0.00048	0.0053	0.0018
Nov 12-14	L	6.8	98.47	24.59	.0160	.0358	.0065	.0011	.00269	.0459	.0075	.00029	.0055	.0014
Nov 26-30	L	7.1	24.50	5.39	.0161	.0337	.0154	.0005	.00412	.0366	.0076	.00025	.0056	.0012
Dec 3-7	L	8.1	26.16	6.95	.0170	.0267	.0134	.0004	.00517	.032	.0077	.00039	.0055	.00144
Dec 10-14	L	8.4	20.94	3.69	.0166	.0173	.011	.0007	.00378	.02575	.0077	.00077	.0057	.00103
1974:														
Jan 2-25	L	5.7	19.73	2.70	.0085	.0416	.0107	.0011	.0114	.0386	.0075	.00034	.0064	.00085
Jan 30-Feb 1	L	7.0	37.75	3.72	.01022	.0398	.0084	.0011	.0066	.040	.0076	.00048	.0061	.00062
Feb 4-6	L	7.1	SO_2 Removal Not Specified		.0159	.0458	.0689	NR	.0025	.0198	.0075	NR	.00597	.0005
Feb 7-8	L	7.2	SO_2 Removal Not Specified		.039	.0438	.1457	NR	.0012	.0116	.0076	.00043	.00656	.00024
Feb 11-15	L	7.2	(18.75)	(1.42)	.090	.0458	.2629	NR	.0011	.0105	.0055	.00039	.00417	.00033
Feb 19-22	L	7.3	(19.13)	(0.59)	.1025	.01875	.2514	NR	.0008	.0078	.0076	.00136	.00648	.00019
Feb 21-Mar 1	L	6.7	(18.67)	(1.40)	.1288	.00021	.2534	NR	.00078	.0074	.0075	NR	.00609	.00046
Mar 4-8	L	7.2	(32.44)	(3.58)	.1175	.0017	.2086	NR	.00125	.00825	.0044	NR	.00305	.00034
Mar 11-14	L	8.4	(31.15)	(5.08)	.118	.0033	.2234	NR	.0017	.00875	.0043	NR	.00295	.00059
Mar 18-22	L	8.3	(33.60)	(2.15)	.0125	.0033	.0169	NR	.00125	.0062	.0053	.0007	.00402	.00024
Mar 25-26	L	7.6	(34.53)	(1.45)	.0073	.0042	.0086	NR	.00047	.0050	.0051	.0006	.00409	.00016
Mar 28-29	L	3.0	(29.95)	(4.09)	.045	.005	.0857	NR	.00094	.0088	.0052	.00023	.00388	.00055
Apr 1-5	L	7.5	(28.03)	(4.55)	.0745	.005	.177	NR	.00094	.0125	.0052	.00039	.00403	.00069
Apr 22-26	L	7.6	(57.85)	(9.45)	.0925	.0204	.200	NR	.00109	.0125	.0051	.00030	.00397	.00064
1975:														
Apr 14-18	LS	5.8	(4.89)	(.48)	.0153	.0104	.04	.008	.0027	.0095	.0056	.0015	.0037	.00036
Apr 21-25	LS	5.9	(6.32)	(.79	.0193	.0038	.039	.0083	.0023	.0086	.0054	.0018	.0037	.00039
Apr 28-May 2	LS	5.7	(6.07)	(.90)	.0345	.0108	.0826	.0081	.0015	.0064	.0052	.0013	.0032	.00048
May 5-9	LS	5.8	(3.77)	(.21)	.0355	.0138	.0869	.0066	.0017	.0082	.0051	.00134	.0035	.0002
May 12-16	LS	5.4	(3.55)	(.36)	.0448	.0175	.102	.0055	.0044	.01663	.0050	.00048	.0038	.00038
May 19-23	LS	5.6	(3.26)	(.62)	.0398	.0196	.0934	.0041	.0016	.0174	.0051	.00134	.0032	.00064

TABLE 3-2 - REPORTED SEALED HOLD TANK DATA - EPA/RTP AND LG&E TEST RESULTS

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Run Date	Feed	pH	Sulfite PPT Rate* (gmole/gm-min) $\times 10^6$	Sulfate PPT Rate* (gmole/gm-min) $\times 10^6$	Hold Tank Liquid Composition (mole/ℓ)						Solid Composition (gmole/gm)			
					Ca	Mg	Cl	CO_2	SO_2	SO_3	Ca	CO_2	SO_2	SO_3
1975 (cont.)														
Jun 2-6	LS	5.4	(1.08)	(0.27)	0.0405	0.0183	0.080	0.0055	0.0034	0.0178	0.0052	0.00043	0.0035	0.00085
Jun 9-13	LS	5.4	(19.64)	(3.74)	.0283	.0296	.083	.0083	.0057	.0174	.0053	.00093	.0037	.00069
Jun 16-20	LS	6.0	(8.56)	(.69)	.0243	.0163	.093	.0071	.0018	.0089	.0051	.00223	.0026	.0002
Jun 23-27	LS	5.9	(8.15)	(1.33)	.0239	.0188	.042	.0077	.0031	.0191	.0052	.00136	.0032	.00051
Jun 30-Jul 3	LS	5.5	(11.26)	(2.47)	.031	NR	.091	.0078	.0018	.0098	.0052	.00168	.0031	.00068
Jul 7-11	LS	5.7	(26.93)	(3.33)	.0249	NR	.076	.0077	.0024	.0078	.0053	.00191	.00298	.00038
LG&E DATA 1973:														
Nov 28	L	8.0	5.00	0.63	.0099	.0046	.01	NR	.001	.0045	.0070	.0008	.0057	.00029
Nov 29	L	8.0	6.52	.32	.0105	.0047	.01	NR	.0008	.0061	.0067	.0008	.0056	.00029
Nov 30	L	7.7	6.39	.17	.0100	.0050	.01	NR	.0010	.0062	.0067	.0006	.0056	.00033

L - Lime

LS - Limestone

NR - Not Reported

* Precipitation rate calculations are based upon hold tank inlet and outlet liquid phase analyses where possible. Data shown in parentheses are for runs in which hold tank inlet analyses were not given. These data are net precipitation rates calculated from SO_2 pick-up and oxidation rate measurements as discussed in Section 2.0.

TABLE 3-3

CALCULATED SEALED HOLD TANK DATA - EPA/RTP AND LG&E TEST RESULTS

Run Date	Feed	pH	Sulfite PPT Rate* (gmole/gm-min) $\times 10^6$	Sulfate PPT Rate* (gmole/gm-min) $\times 10^6$	Solution Activities** $a_{Ca^{++}}$ $(\times 10^3)$	$a_{Mg^{++}}$ $(\times 10^3)$	a_{Cl^-} $(\times 10^2)$	$a_{CO_3^{-2}}$ $(\times 10^7)$	$a_{SO_3^{-2}}$ $(\times 10^4)$	$a_{SO_4^{-2}}$ $(\times 10^3)$	Mole Fraction in Solids SO_2	SO_3	Relative Saturations** $CaSO_3 \cdot \frac{1}{2}H_2O$	$CaSO_4 \cdot 2H_2O$	$CaSO_4 \cdot \frac{1}{2}H_2O$
EPA/RTP DATA 1973:															
Jan 18	LS	6.3	10.14	18.02	2.92	6.63	----	1.97	1.51	7.38	NR	NR	6.67	0.992	0.468
Jan 19	LS	6.2	2.27	1.64	3.15	5.16	----	2.00	1.42	7.15	NR	NR	6.75	1.04	.491
Jan 23	LS	6.3	12.56	5.64	2.89	6.15	----	2.31	1.34	8.18	NR	NR	5.84	1.09	.515
Feb 5-10	LS	6.3	10.95	4.03	3.37	6.43	----	3.66	1.11	6.52	NR	NR	5.65	1.01	.477
Feb 13-22	LS	6.4	20.24	5.08	3.21	4.37	----	5.12	1.15	6.43	NR	NR	5.58	.948	.448
Mar 5-7	LS	6.4	6.33	1.87	4.26	2.47	-----	6.14	0.76	4.20	NR	NR	4.93	.825	.389
Mar 12-13	LS	6.6	9.03	.62	2.45	2.87	-----	9.86	1.18	2.33	NR	NR	4.35	.263	.124
Mar 14-15	LS	6.6	9.09	2.57	2.80	3.86	-----	8.70	1.05	2.87	NR	NR	4.43	.370	.175
Mar 29-Apr 4	LS	6.5	20.96	5.56	3.41	3.81	-----	5.82	1.09	4.09	NR	NR	5.64	.642	.303
Apr 9-11	LS	6.6	23.86	3.85	2.94	4.49	-----	8.90	1.40	4.03	NR	NR	6.21	.545	.257
May 14-Jun 6	LS	6.2	35.01	4.33	1.87	7.70	-----	2.44	1.99	3.99	NR	NR	5.65	.343	.162
Jun 25-29	LS	5.8	22.55	2.78	0.52	10.6	-----	0.56	2.05	3.99	NR	NR	1.60	.947	.447
July 2-6	LS	6.3	47.54	10.78	1.66	6.50	-----	3.94	2.69	4.99	NR	NR	6.73	.380	.179
July 17-20	LS	6.2	21.96	2.21	0.5	5.83	-----	3.26	4.43	3.34	NR	NR	3.34	.077	.036
1974:															
Jan 28-Feb 1	LS	5.6	(15.66)	(2.75)	7.89	7.7	4.12	----	0.65	2.56	NR	NR	7.71	.927	.438
Feb 4-8	LS	5.2	(17.16)	(3.78)	4.66	27.59	3.85	----	0.53	3.01	NR	NR	3.72	.642	.303
Feb 11-14	LS	5.9	(17.32)	(3.06)	1.39	26.74	3.91	----	1.37	3.34	NR	NR	2.86	.212	.100
Feb 14-15	LS	6.1	(28.30)	(2.14)	1.76	30.08	3.83	----	1.81	4.87	NR	NR	4.81	.393	.185
Feb 19-22	LS	5.9	(26.67)	(2.65)	2.38	31.79	10.19	----	1.89	6.02	NR	NR	6.81	.653	.308
Feb 25-Mar 1	LS	5.9	(26.25)	(3.91)	8.17	21.22	11.93	----	0.48	2.15	NR	NR	5.93	.804	.379
1973:															
Oct 16-19	L	6.0	64.56	9.61	4.09	1.45	0.61	0.13	0.35	4.82	0.873	0.127	2.19	.910	.430
Oct 19-23	L	6.7	77.32	13.67	2.33	5.62	0.75	1.53	1.74	5.31	.852	.148	6.10	.569	.269
Oct 29-Nov 2	L	7.0	30.18	3.42	0.99	10.31	0.99	4.46	2.76	5.74	.897	.103	4.12	.261	.123

TABLE 3-3 - CALCULATED SEALED HOLD TANK DATA - EPA/RTP AND LG&E TEST RESULTS (cont.)

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Run Date	Feed	pH	Sulfite PPT Rate* (gmole/gm-min) ×10⁶	Sulfate PPT Rate* (gmole/gm-min) ×10⁶	Solution Activities** $^{a}Ca^{++}$ (×10³)	$^{a}Mg^{++}$ (×10³)	$^{a}Cl^{-}$ (×10²)	$^{a}CO_3^{-2}$ (×10⁷)	$^{a}SO_3^{-2}$ (×10⁴)	$^{a}SO_4^{-2}$ (×10³)	Mole Fraction in Solids SO_2	SO_3	Relative Saturations** $CaSO_3 \cdot \frac{1}{2}H_2O$	$CaSO_4 \cdot 2H_2O$	$CaSO_4 \cdot \frac{1}{2}H_2O$
1973 (cont.)															
Nov 5-8	L	7.3	77.30	25.82	2.73	8.65	0.66	5.79	1.59	6.34	0.747	0.253	6.54	0.797	0.376
Nov 12-14	L	6.8	98.47	24.58	3.16	7.54	0.49	2.62	1.00	6.74	.797	.203	4.79	.979	.462
Nov 26-30	L	7.1	24.50	5.39	3.34	7.84	1.17	2.56	1.64	5.30	.824	.176	8.24	.813	.384
Dec 3-7	L	8.1	26.16	6.95	3.46	6.24	1.03	19.69	2.41	5.15	.793	.207	12.51	.815	.385
Dec 10-14	L	8.4	20.94	3.69	3.65	4.28	0.86	64.8	1.91	4.81	.847	.153	10.53	.810	.382
1974:															
Jan 2-25	L	5.7	19.73	2.70	1.77	9.61	0.81	0.007	1.39	5.43	.883	.117	3.71	.442	.209
Jan 30-Feb 1	L	7.0	37.75	3.72	1.86	8.49	0.64	4.49	3.07	6.01	.908	.092	8.63	.514	.243
Feb 4-6	L	7.1	SO_2 Removal Not Specified		4.05	13.99	5.03	----	0.72	2.01	.923	.077	4.42	.374	.177
Feb 7-8	L	7.2	SO_2 Removal Not Specified		9.99	14.12	10.12	----	0.22	0.92	.965	.035	3.33	.423	.200
Feb 11-15	L	7.2	(18.75)	(1.42)	20.90	13.98	17.16	----	0.13	0.62	.927	.073	3.92	.586	.277
Feb 19-22	L	7.3	(19.13)	(0.59)	24.46	5.88	16.57	----	0.088	0.52	.972	.028	3.24	.575	.271
Feb 21-Mar 1	L	6.7	(18.67)	(1.40)	30.52	0.06	16.62	----	0.070	0.49	.930	.070	3.23	.685	.323
Mar 4-8	L	7.2	(32.44)	(3.58)	28.30	0.53	13.87	----	0.12	0.59	.90	.10	5.34	.756	.357
Mar 11-14	L	8.4	(31.15)	(5.08)	28.06	1.02	14.80	----	0.18	0.61	.833	.167	7.47	.784	.370
Mar 18-22	L	8.3	(33.60)	(2.15)	4.52	1.32	1.39	----	0.65	1.53	.944	.056	4.44	.319	.151
Mar 25-26	L	7.6	(34.53)	(1.45)	2.99	1.83	0.73	----	0.31	1.41	.962	.038	1.42	.195	.092
Mar 28-29	L	8.0	(29.95)	(4.09)	13.09	1.74	6.28	----	0.19	1.07	.876	.124	3.74	.646	.305
Apr 1-5	L	7.5	(28.03)	(4.55)	18.67	1.56	12.21	----	0.14	1.15	.854	.146	3.85	.978	.462
Apr 22-26	L	7.6	(57.85)	(9.45)	22.12	6.27	13.39	----	0.13	0.88	.861	.139	4.31	.890	.420
1975:															
Apr 14-18	LS	5.8	(4.89)	(.48)	4.82	3.70	3.13	0.77	0.38	1.72	.911	.089	2.75	.381	.180
Apr 21-25	LS	5.9	(6.32)	(.79	6.18	1.37	3.07	1.17	0.36	1.71	.905	.095	3.38	.485	.229
Apr 28-May 2	LS	5.7	(6.07)	(.90)	10.40	3.91	6.10	0.51	0.14	0.80	.869	.131	2.20	.380	.179
May 5-9	LS	5.8	(3.77)	(.21)	10.31	4.83	6.37	0.61	0.18	0.97	.946	.054	2.79	.460	.217
May 12-16	LS	5.4	(3.55)	(.36)	11.58	5.41	7.32	0.10	0.24	1.77	.909	.091	4.27	.940	.444
May 19-23	LS	5.6	(3.26)	(.62)	10.46	6.06	6.75	0.17	0.13	1.90	.833	.167	1.98	.910	.430

TABLE 3-3 - CALCULATED SEALED HOLD TANK DATA - EPA/RTP AND LG&E TEST RESULTS

					Solution Activities**						Mole Fraction in Solids		Relative Saturations**		
Run Date	Feed	pH	Sulfite PPT Rate* (gmole/gm-min) ×10^6	Sulfate PPT Rate* (gmole/gm-min) ×10^6	^{a}Ca^{++} (×10^3)	^{a}Mg^{++} (×10^3)	^{a}Cl$^-$ (×10^2)	^{a}CO$_3^{-2}$ (×10^7)	^{a}SO$_3^{-2}$ (×10^4)	^{a}SO$_4^{-2}$ (×10^3)	SO$_2$	SO$_3$	CaSO$_3$·½H$_2$O	CaSO$_4$·2H$_2$O	CaSO$_4$·½H$_2$O
1975 (cont.)															
Jun 2-6	LS	5.4	(1.08)	(0.27)	10.66	5.65	5.81	0.10	0.19	1.98	0.805	0.195	3.11	0.968	0.457
Jun 9-13	LS	5.4	(19.64)	(3.74)	7.40	9.18	6.03	0.16	.34	1.88	.813	.187	3.77	.638	.301
Jun 16-20	LS	6.0	(8.56)	(.69)	7.00	5.62	6.89	1.62	.28	1.17	.930	.070	2.92	.377	.178
Jun 23-27	LS	5.9	(8.15)	(1.33)	6.35	5.65	3.18	1.06	.44	2.69	.863	.137	4.22	.785	.370
Jun 30-Jul 3	LS	5.5	(11.26)	(2.47)	9.17	----	6.84	0.22	.13	1.61	.820	.180	1.85	.679	.320
Jul 7-11	LS	5.7	(26.93)	(3.33)	7.72	----	5.82	0.50	.26	1.45	.887	.113	3.06	.515	.243
LG&E DATA 1973:															
Nov 28	L	8.0	6.02	0.75	3.91	2.03	.83	---	.60	1.30	.953	.047	2.78	.222	.0873
Nov 29	L	8.0	10.91	0.54	4.04	1.98	.83	---	.46	1.58	.952	.048	2.22	.281	.110
Nov 30	L	7.7	11.81	0.31	3.78	2.08	.83	---	.58	1.61	.946	.054	2.59	.270	.106

L - Lime

LS - Limestone

NS - Not Reported

* Precipitation rate calculations are based upon hold tank inlet and outlet liquid phase analyses where possible. Data shown in parentheses are for runs in which hold tank inlet analyses were not given. These data are net precipitation rates calculated from SO$_2$ pick-up and oxidation rate measurements as discussed in Section 2.0.

** Calculated using Radian aqueous ionic equilibrium program.

4.0 DISCUSSION

As stated earlier, the purpose of this data review was twofold:

1) to define ranges of operating conditions under which coprecipitation is observed to occur,

2) to provide a basis for comparing the results obtained in Radian laboratory experiments with actual scrubber performance.

Key operating parameters which were identified as possibly having an effect on the coprecipitation were the sulfite precipitation rate, relative saturation of calcium sulfate dihydrate, relative saturation of calcium sulfate hemihydrate, chloride concentration, magnesium concentration, and activity of the sulfate ion.

The ranges of these operating conditions under which coprecipitation of sulfate with sulfite was observed in the EPA/RTP field data are as follows:

Sulfite precipitation rate: .001 - .100 $\frac{\text{millimole}}{\text{gm-min}}$

Relative saturation $CaSO_4\cdot 2H_2O$: .07 -1.10

Relative saturation $CaSO_4\cdot \frac{1}{2}H_2O$: .03 - .52

Chloride concentration: .005 - .42 mole/liter

Magnesium concentration: .0005- .70 mole/liter

Sulfate activity: .0005- .0082

Radian's laboratory program was designed to encompass these ranges of operating parameters.

The EPA/RTP, LG&E and Shawnee data were analyzed according to the theoretical framework developed by Philip S. Lowell in Appendix A. This theoretical framework and Radian experimental data suggest that the sulfate mole fraction is best correlated with the relative saturation of calcium sulfate hemihydrate. The results of a graphical analysis of this correlation for the EPA/RTP and LG&E data is shown in Figure B-1.

There is a significant degree of scatter in the data; part of this scatter is very likely due to analytical inaccuracies in the determination of the sulfate content of the solids. Also, correlation of these pilot unit data with liquid phase properties is difficult since a change in one parameter is usually accompanied by other changes. However, the high sulfate content of the solids precipitated in the field limestone runs made at high liquid phase magnesium concentrations cannot be solely explained by analytical inaccuracies. Experimental difficulties associated with the sampling and sample handling of slurries containing high liquid phase magnesium sulfate concentrations can account for some scatter. Additional chemical analyses and characterization of field solids would be required to determine if the high liquid phase magnesium concentrations are having a significant effect on the level of sulfate coprecipitated.

The EPA/RTP pilot plant data do show, as do Radian experimental data, that gypsum unsaturated operation is possible and that the relative saturation of calcium sulfate does affect the sulfate content in the solids even in unsaturated operation.

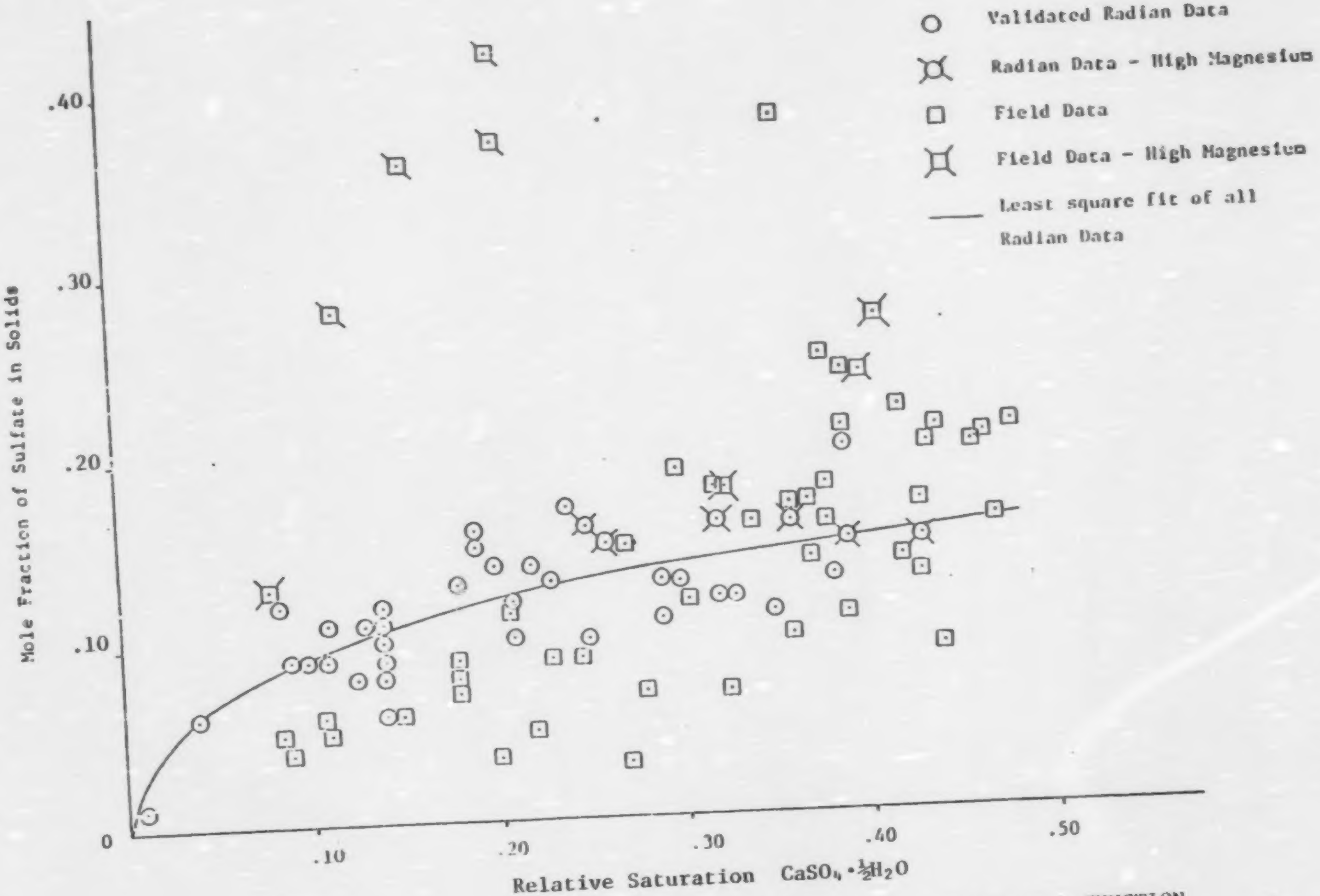

FIGURE B-1 CONCENTRATION OF SULFATE IN THE SOLIDS AS A FUNCTION OF THE $CaSO_4 \cdot \frac{1}{2}H_2O$ RELATIVE SATURATION IN THE AQUEOUS PHASE FOR FIELD DATA AND RADIAN DATA

Experimental data from EPA's alkali scrubbing test facility located at TVA's Shawnee Power Station were also examined. The sulfate content of the solids has been compared with the liquid phase relative saturation of calcium sulfate as a function of time for both lime and limestone runs. This allows solids residence time to be included in the analysis as the residence time of the solids is in the order of days. Graphical results of these comparisons in the TCA-limestone runs for the time period June through December 1975 are presented in Figures B-2 to B-9. Comparisons of the sulfate mole fraction with the relative saturation of calcium sulfate dihydrate for the venturi/spray tower-lime runs are presented in Figures B-10 to B-15 and encompass the same time period as the TCA-limestone runs.

The solids residence time in the system is the slurry volume of the system divided by the rate of slurry withdrawal from the system. This usually varies from many hours to several days. A sample of slurry is, therefore, a composite of what has happened over the last several days. For a chemical analysis of the solids to be representative of the liquid surrounding them at the sampling time, the liquid must have been constant for at least one residence time and preferably longer.

One other factor is significant. Gypsum will probably be formed when its relative saturation is greater than 1.0. Just as it takes time (1-2 days) to grow a large gypsum crystal, so it takes time to dissolve one. Those periods of time during which the relative saturation of gypsum was greater than one, and for a day or so after, the sulfate in the solids will consist of both solid solution sulfate and gypsum sulfate. A total solid sulfate analysis will not be an accurate description of what is presently being precipitated from solution.

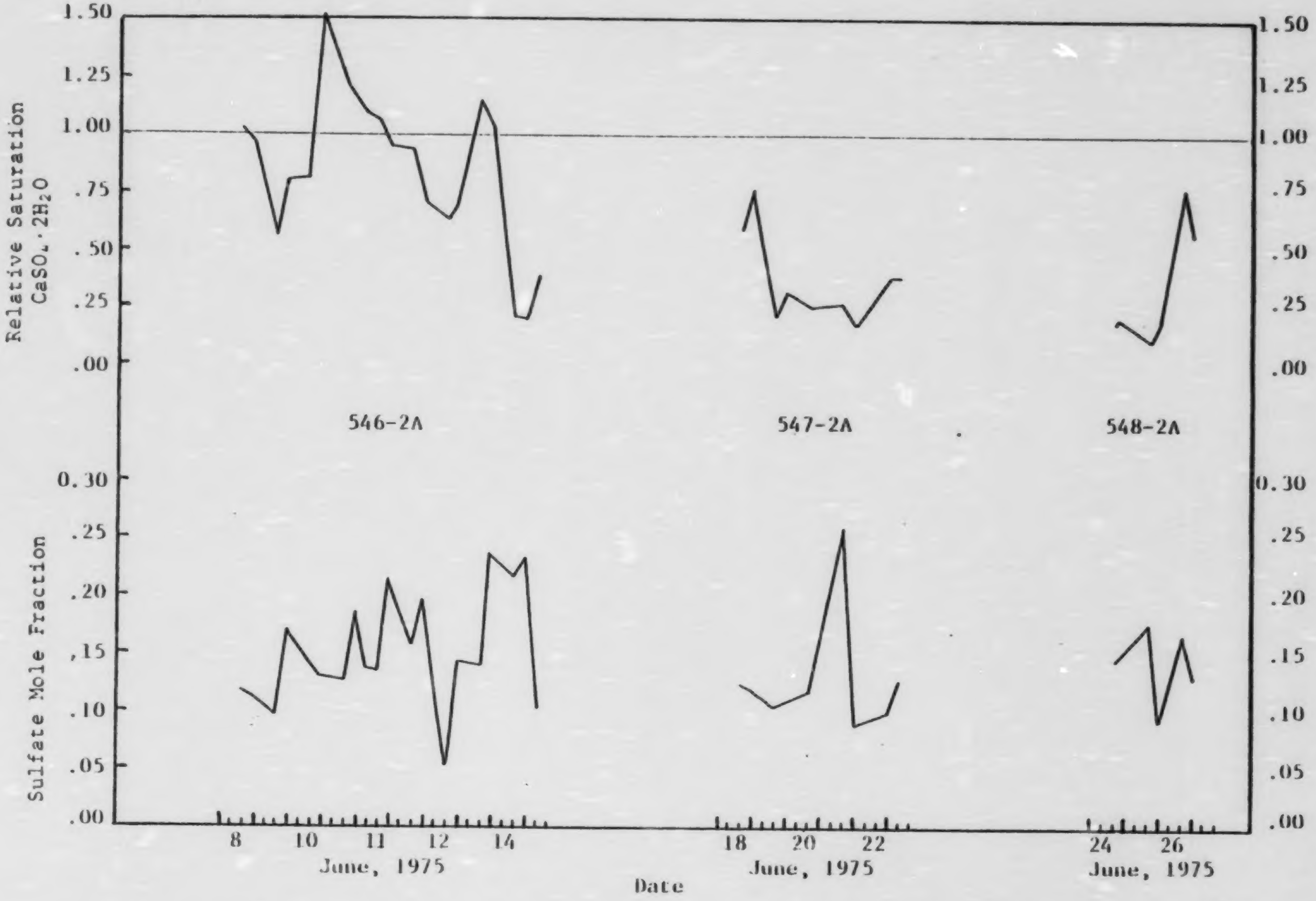

FIGURE B-2. RELATIONSHIP BETWEEN SULFATE MOLE FRACTION AND GYPSUM RELATIVE SATURATION FOR SHAWNEE TCA-LIMESTONE RUNS

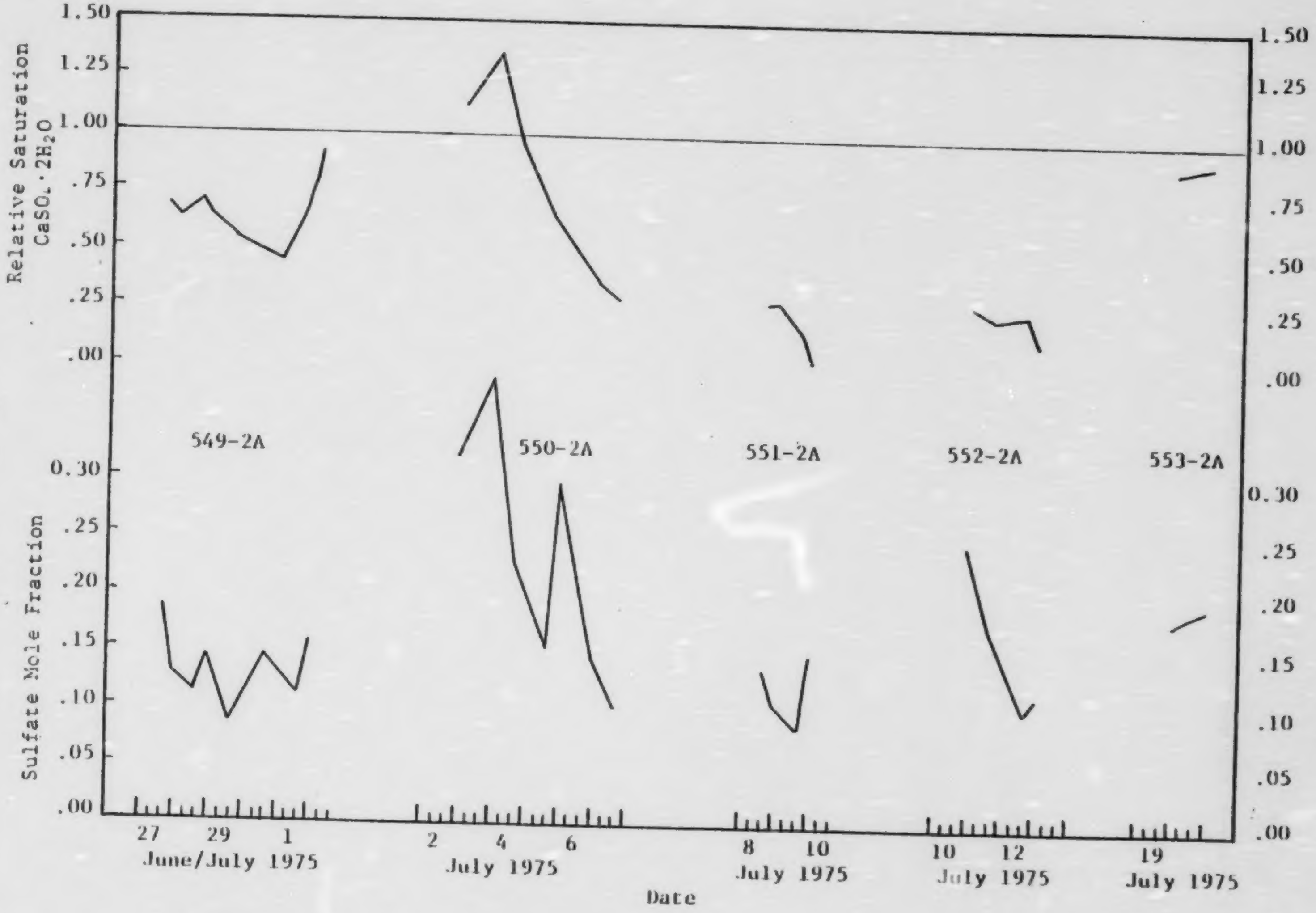

FIGURE B-3. RELATIONSHIP BETWEEN SULFATE MOLE FRACTION AND GYPSUM RELATIVE SATURATION FOR SHAWNEE TCA-LIMESTONE RUNS

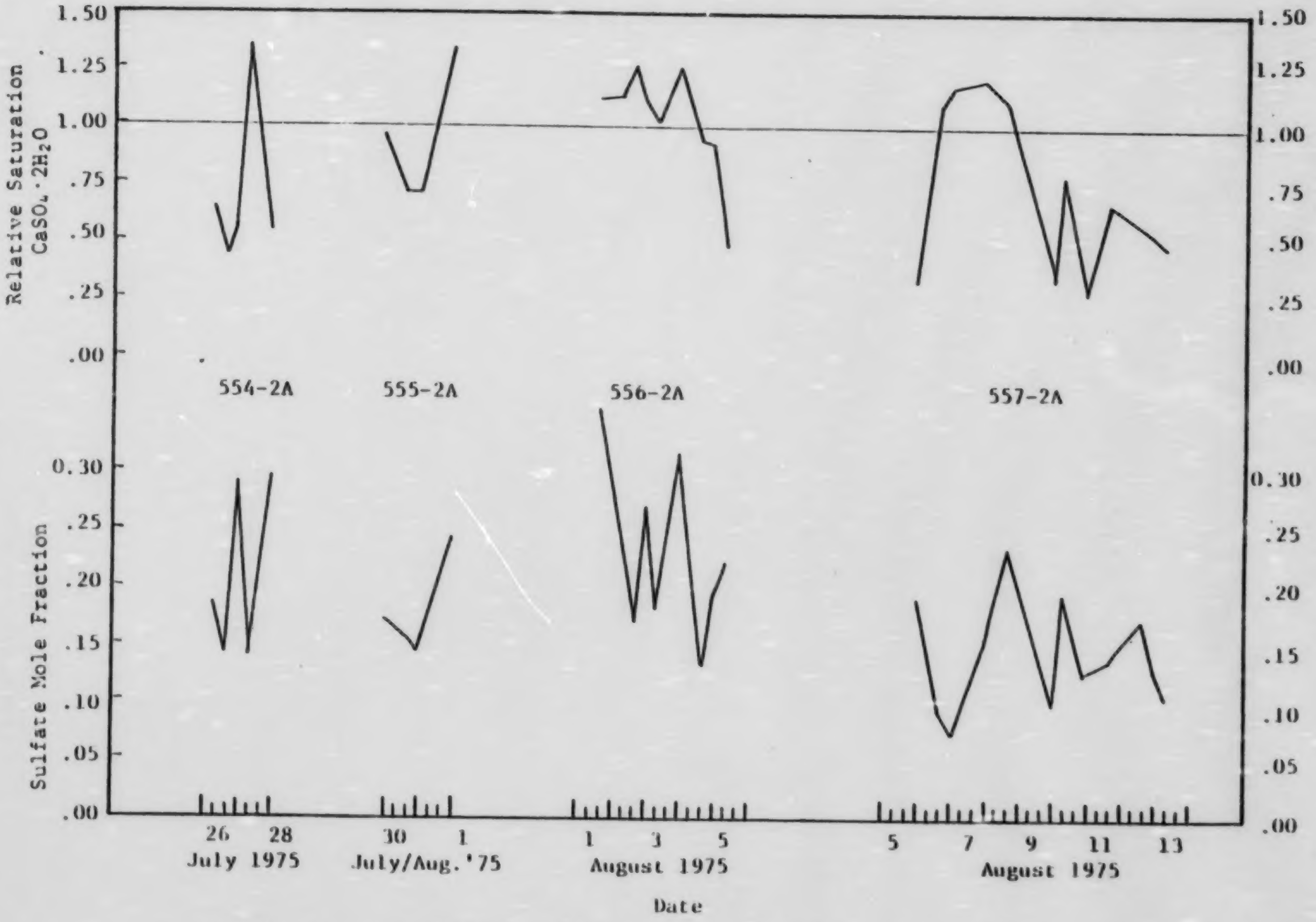

FIGURE B-4. RELATIONSHIP BETWEEN SULFATE MOLE FRACTION AND GYPSUM RELATIVE SATURATION FOR SHAWNEE TCA-LIMESTONE RUNS

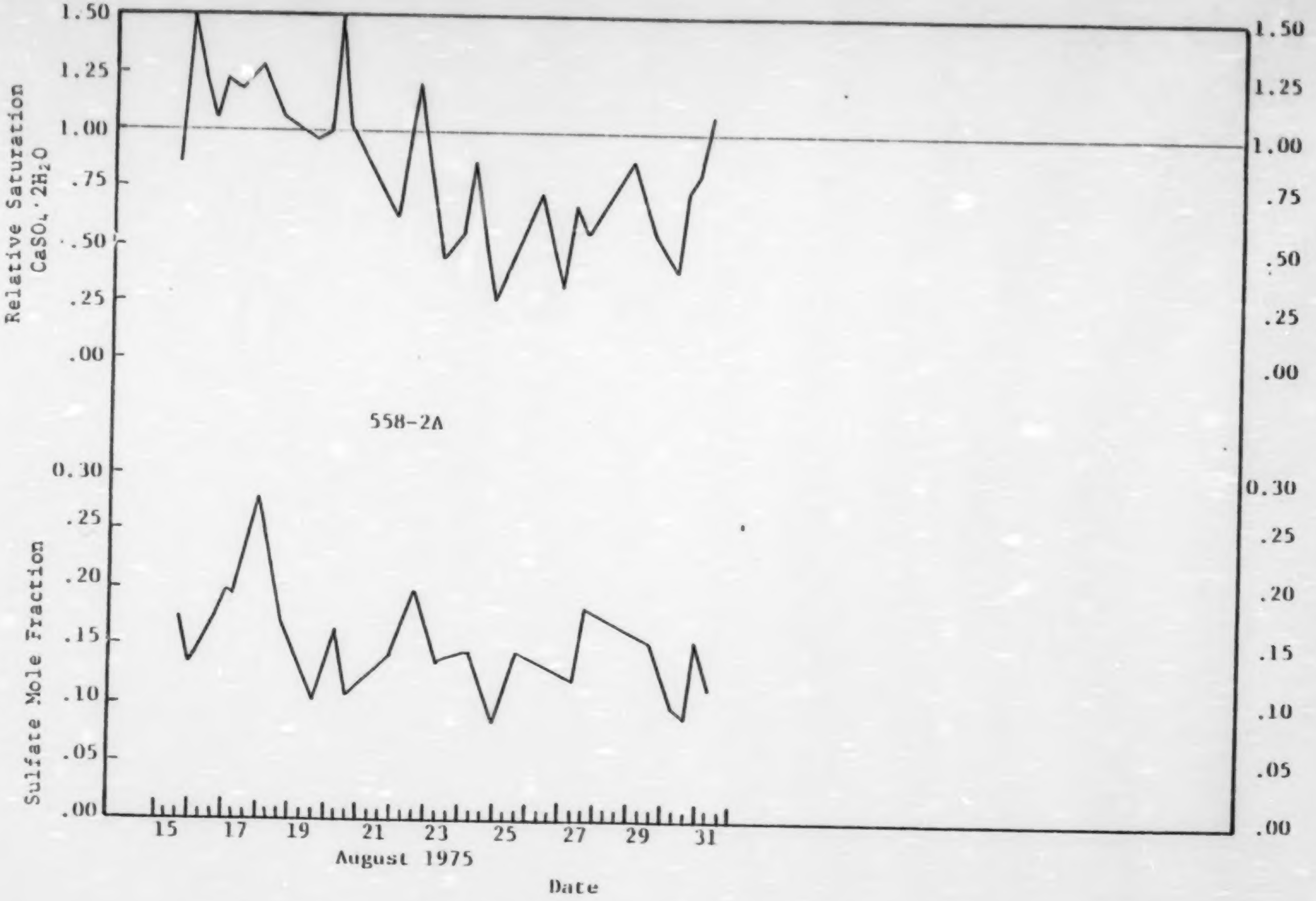

FIGURE B-5. RELATIONSHIP BETWEEN SULFATE MOLE FRACTION AND GYPSUM RELATIVE SATURATION FOR SHAWNEE TCA-LIMESTONE RUNS

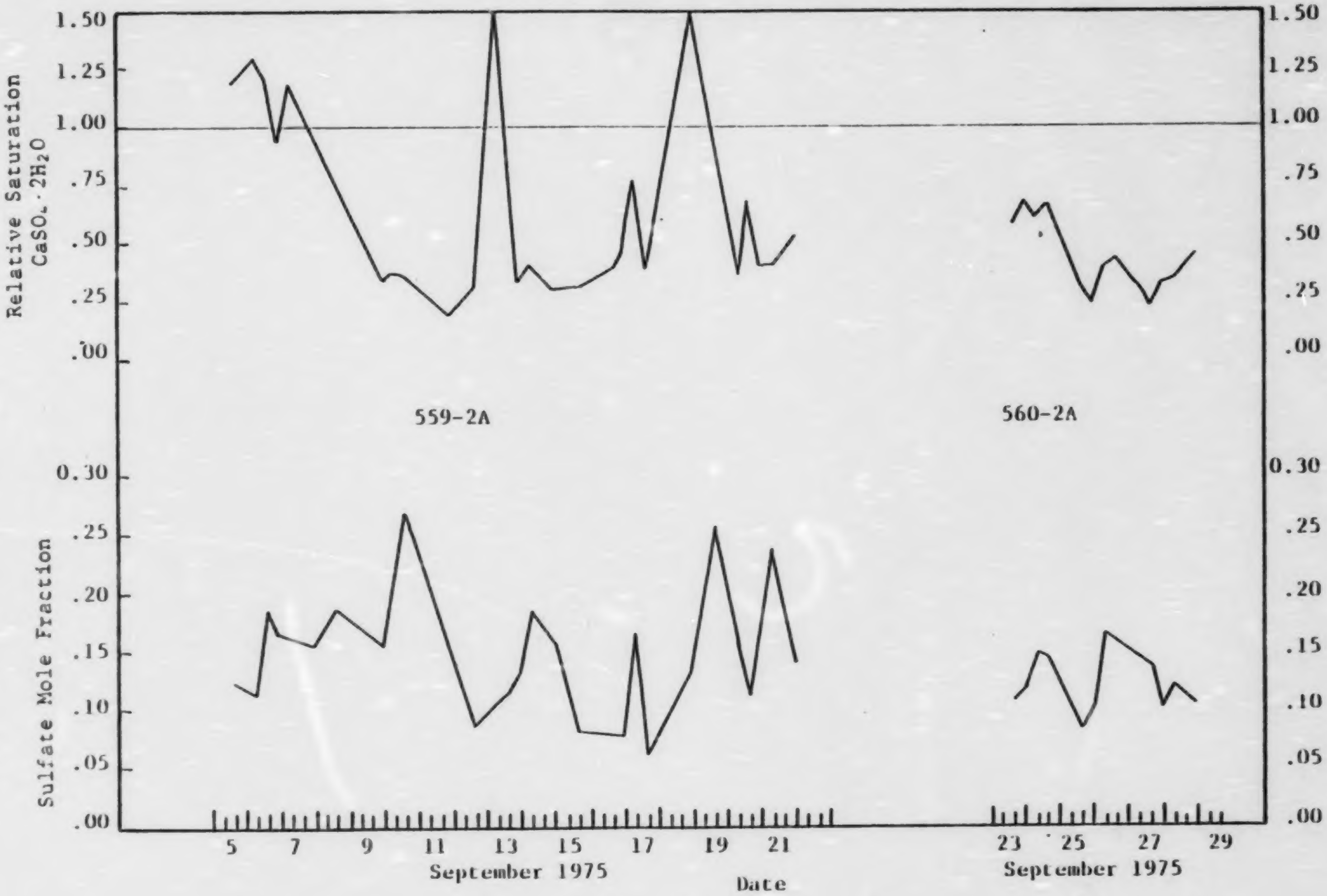

FIGURE B-6. RELATIONSHIP BETWEEN SULFATE MOLE FRACTION AND GYPSUM RELATIVE SATURATION FOR SHAWNEE TCA-LIMESTONE RUNS

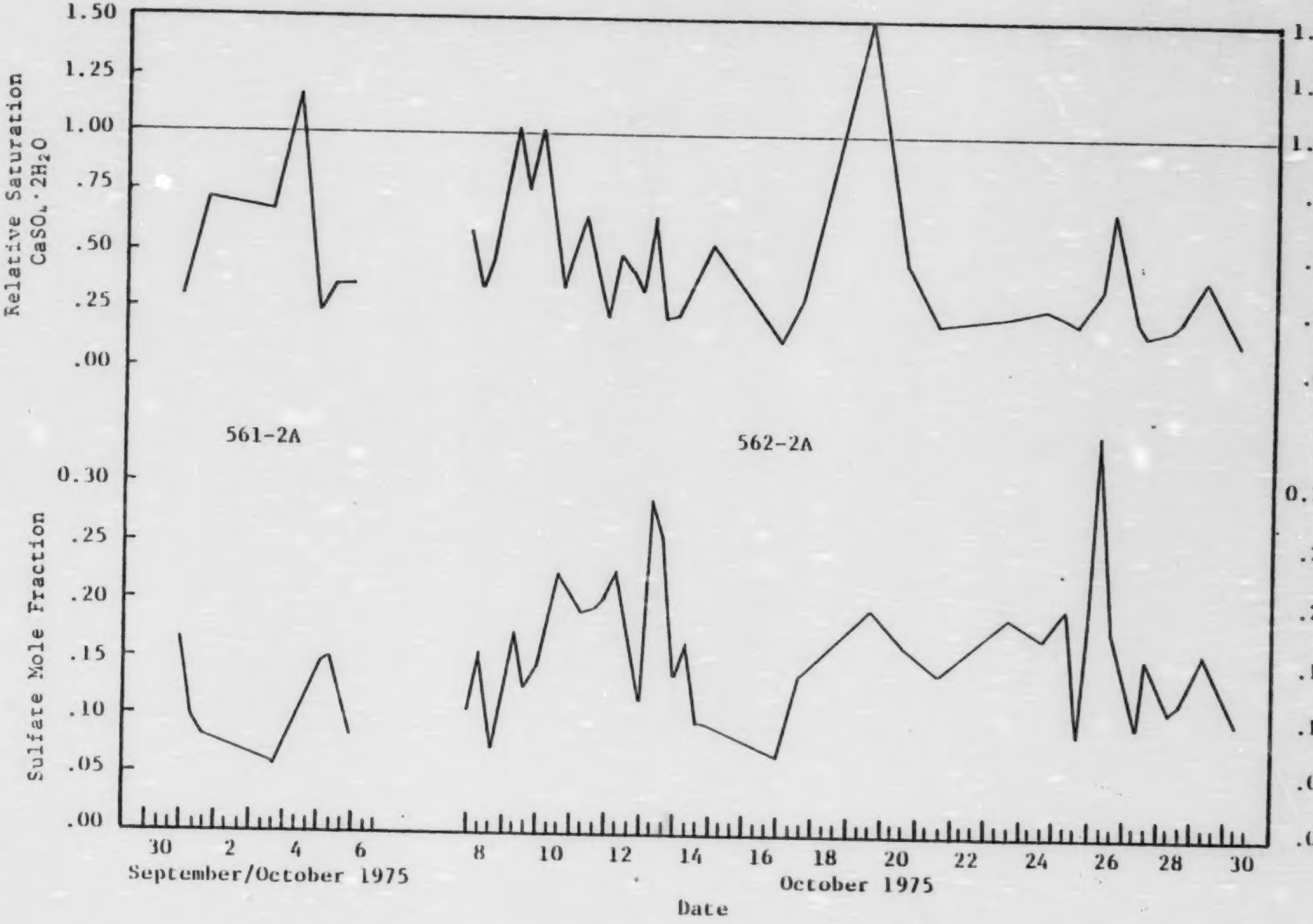

FIGURE B-7. RELATIONSHIP BETWEEN SULFATE MOLE FRACTION AND GYPSUM RELATIVE SATURATION FOR SHAWNEE TCA-LIMESTONE RUNS

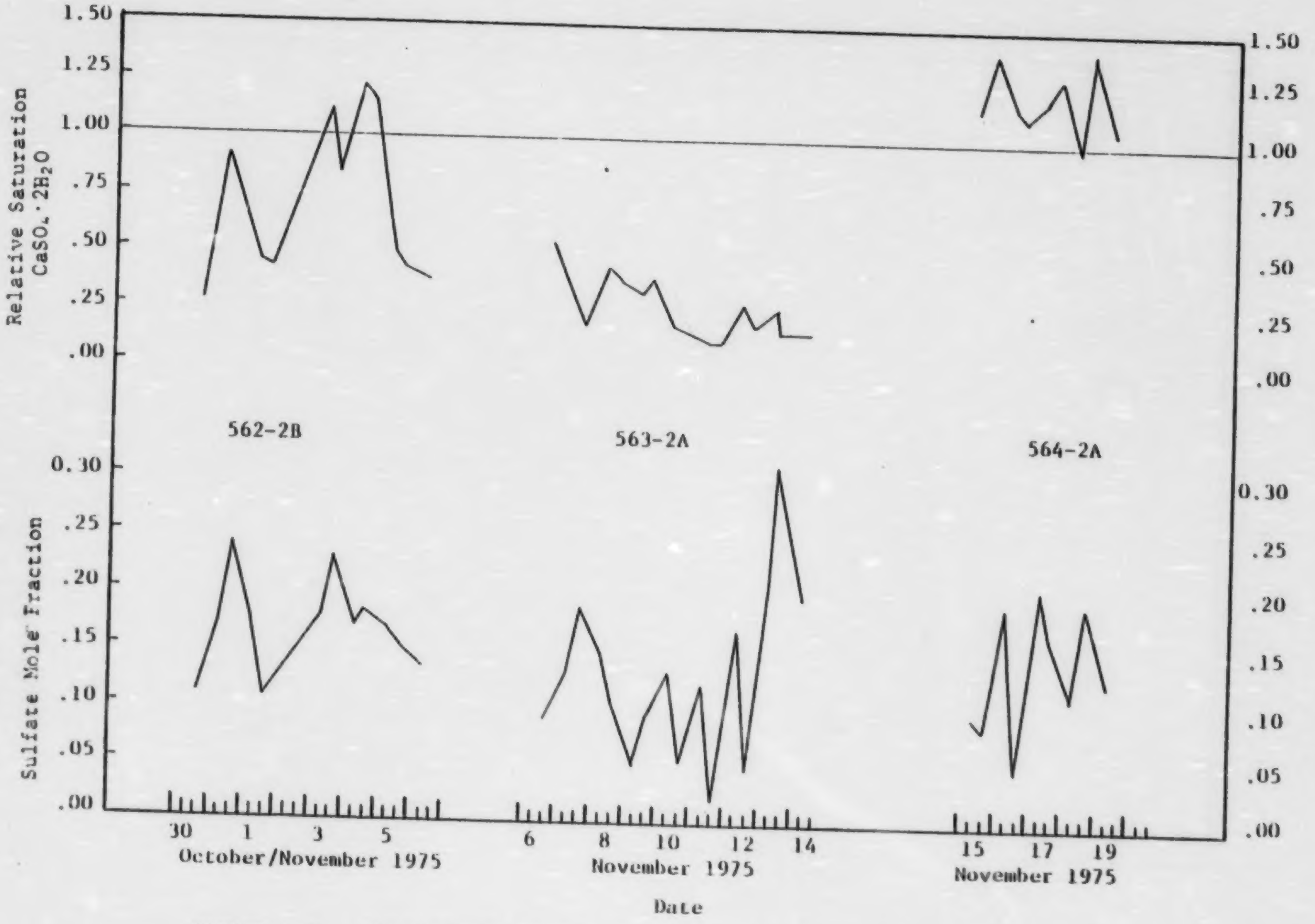

FIGURE B-8. RELATIONSHIP BETWEEN SULFATE MOLE FRACTION AND GYPSUM RELATIVE SATURATION FOR SHAWNEE TCA-LIMESTONE RUNS

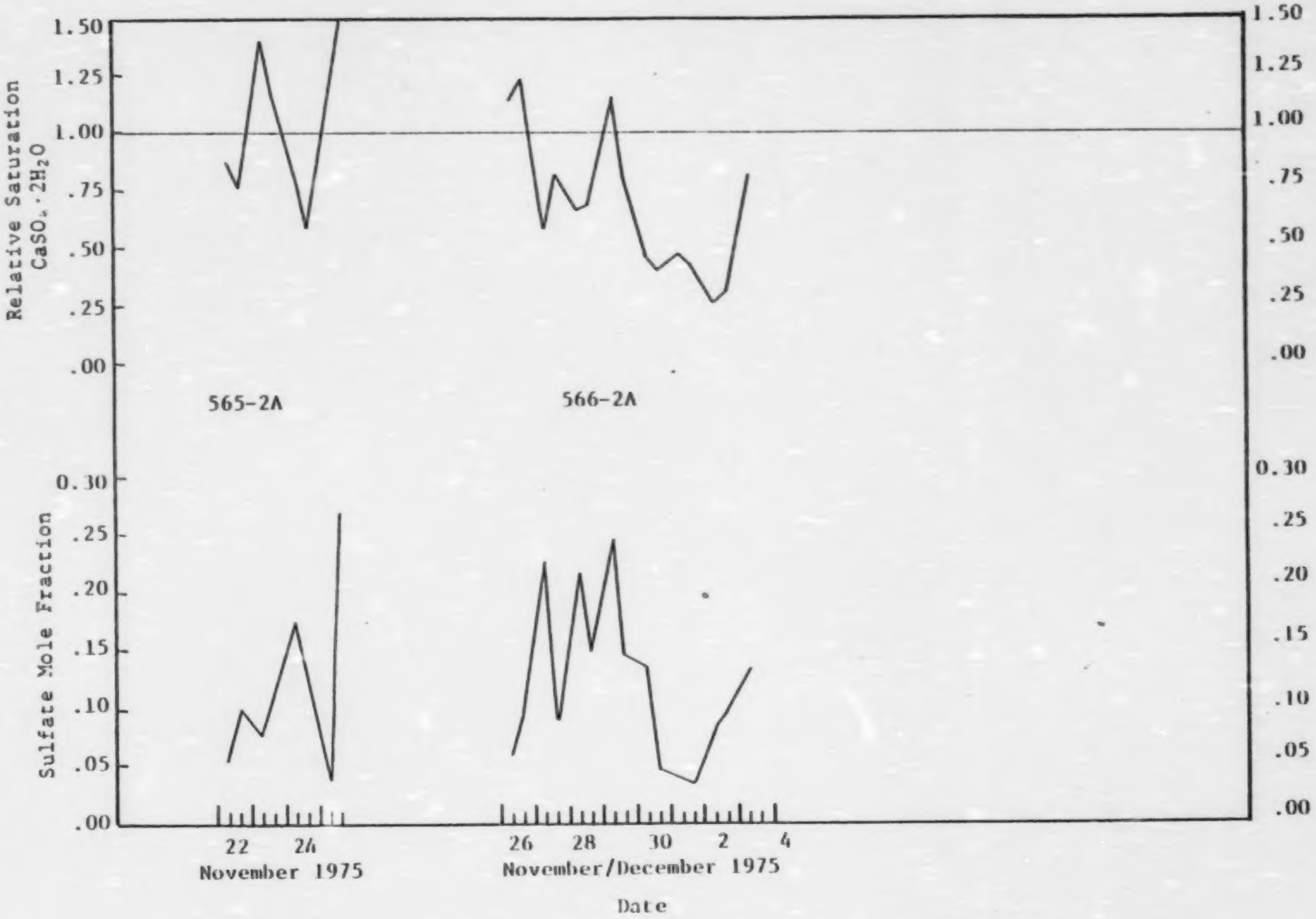

FIGURE B-9. RELATIONSHIP BETWEEN SULFATE MOLE FRACTION AND GYPSUM RELATIVE SATURATION FOR SHAWNEE TCA-LIMESTONE RUNS

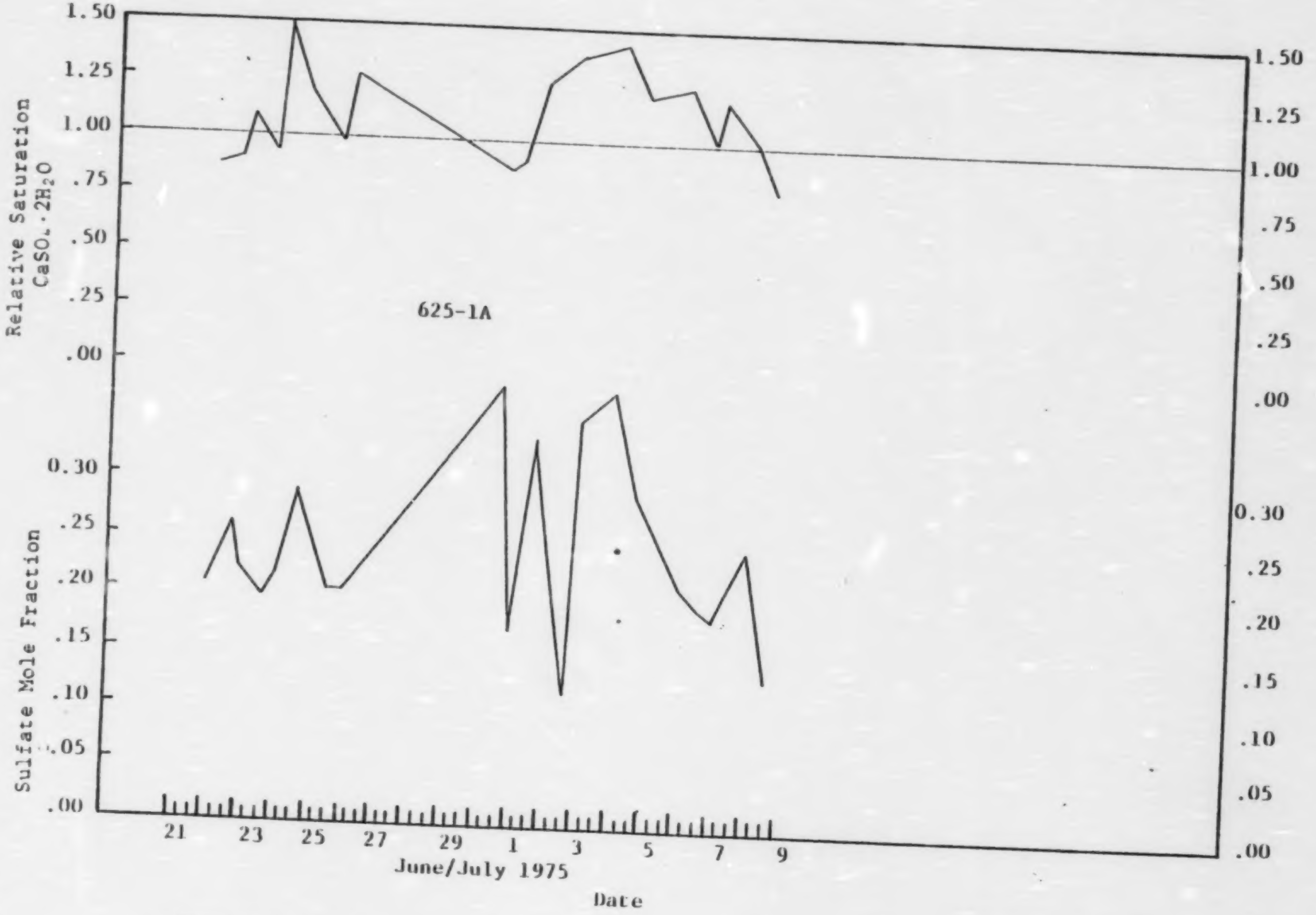

FIGURE B-10. RELATIONSHIP BETWEEN SULFATE MOLE FRACTION AND GYPSUM RELATIVE SATURATION FOR SHAWNEE VENTURI/SPRAY TOWER-LIME RUNS

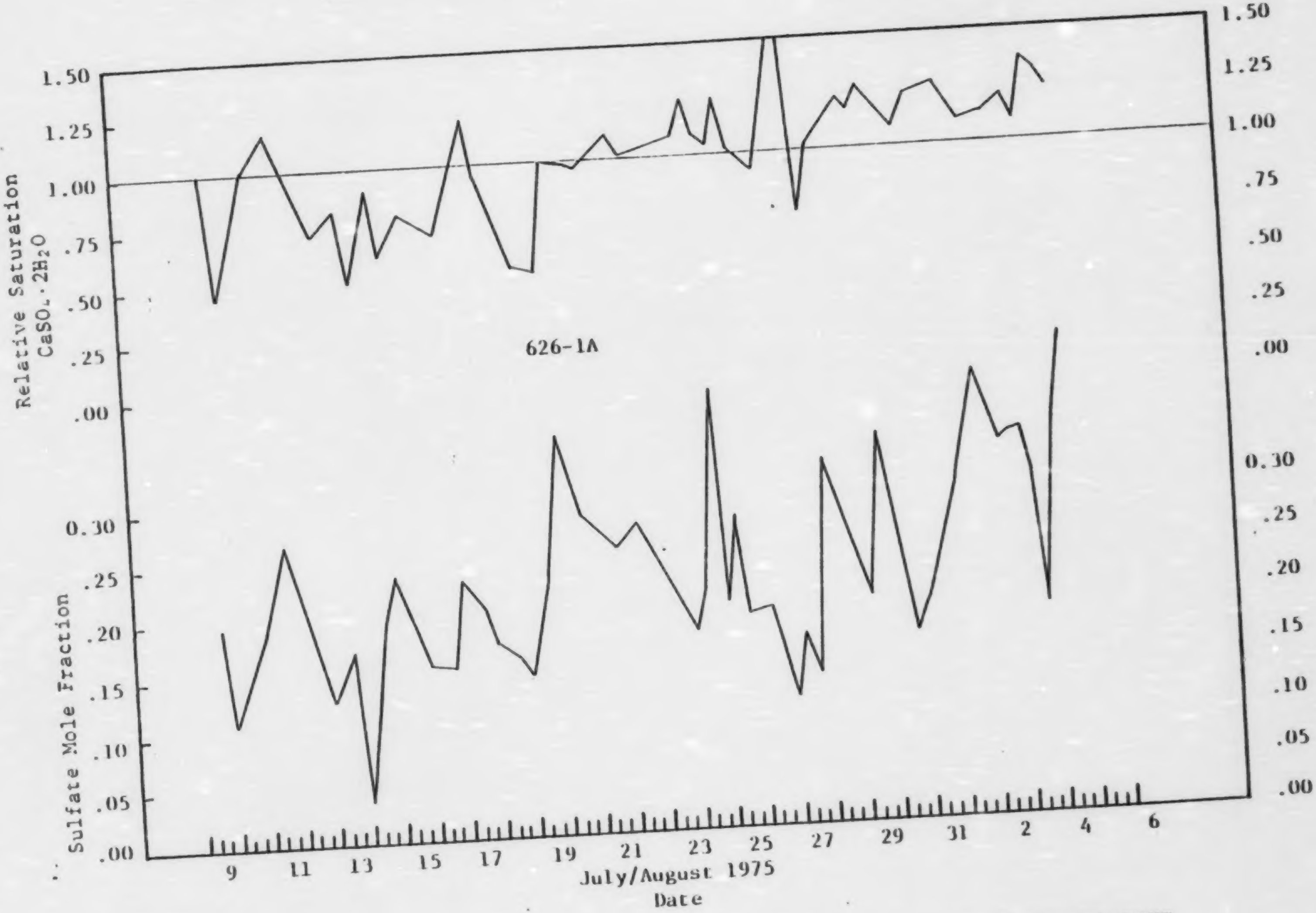

FIGURE B-11. RELATIONSHIP BETWEEN SULFATE MOLE FRACTION AND GYPSUM RELATIVE SATURATION FOR SHAWNEE VENTURI/SPRAY TOWER-LIME RUNS

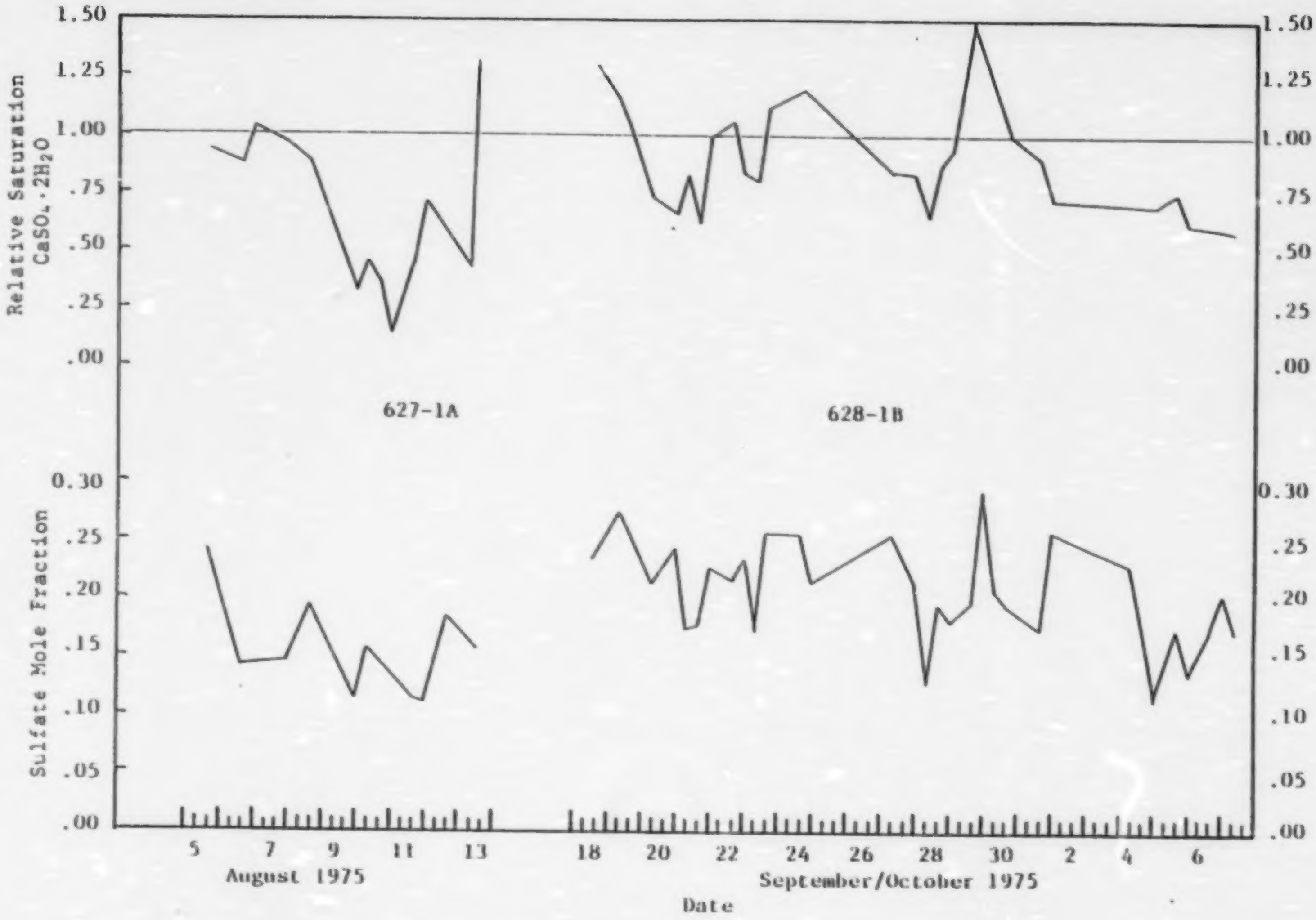

FIGURE B-12. RELATIONSHIP BETWEEN SULFATE MOLE FRACTION AND GYPSUM RELATIVE SATURATION FOR SHAWNEE VENTURI/SPRAY TOWER-LIME RUNS

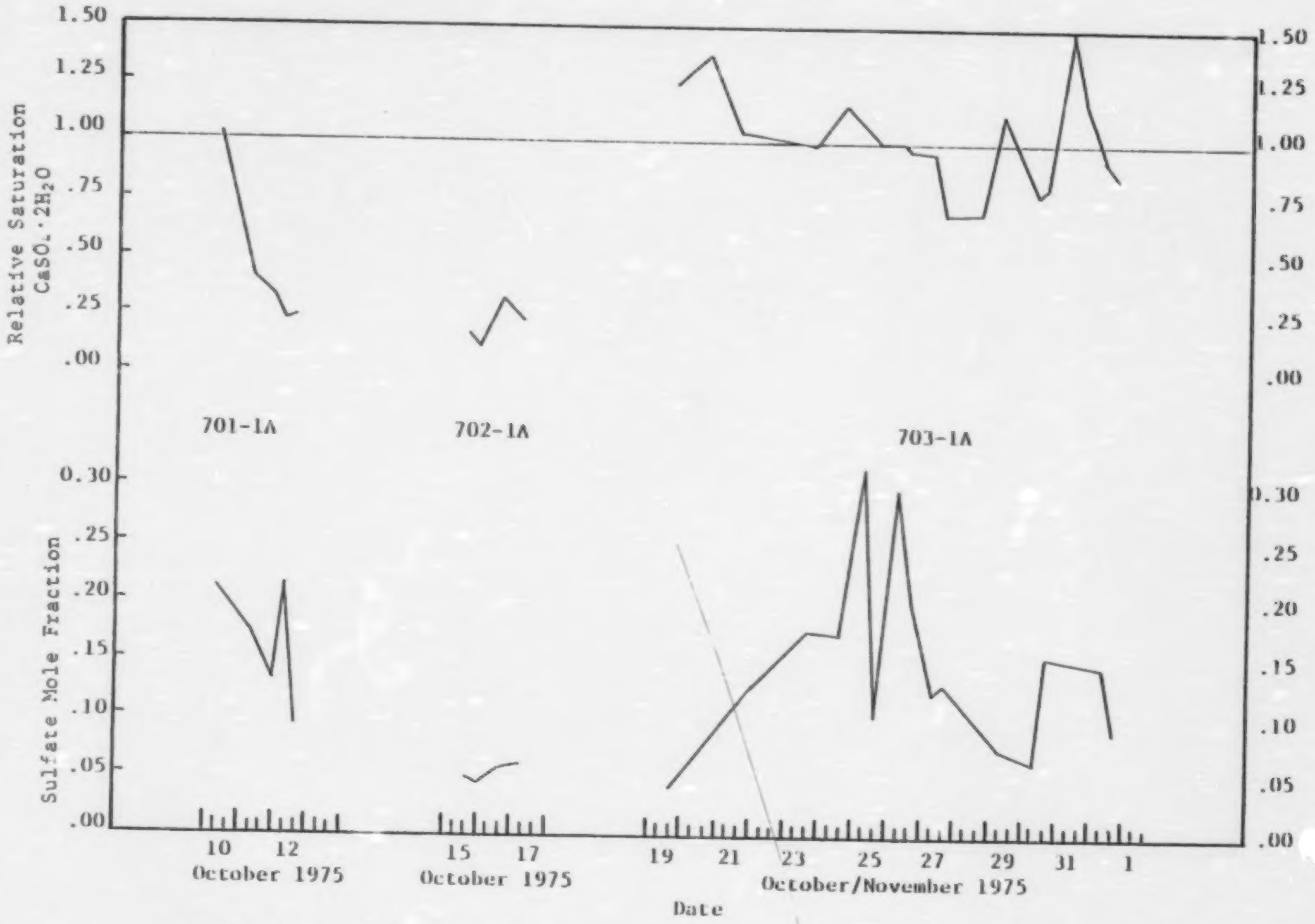

FIGURE B-13. RELATIONSHIP BETWEEN SULFATE MOLE FRACTION AND GYPSUM RELATIVE SATURATION FOR SHAWNEE VENTURI/SPRAY TOWER-LIME RUNS

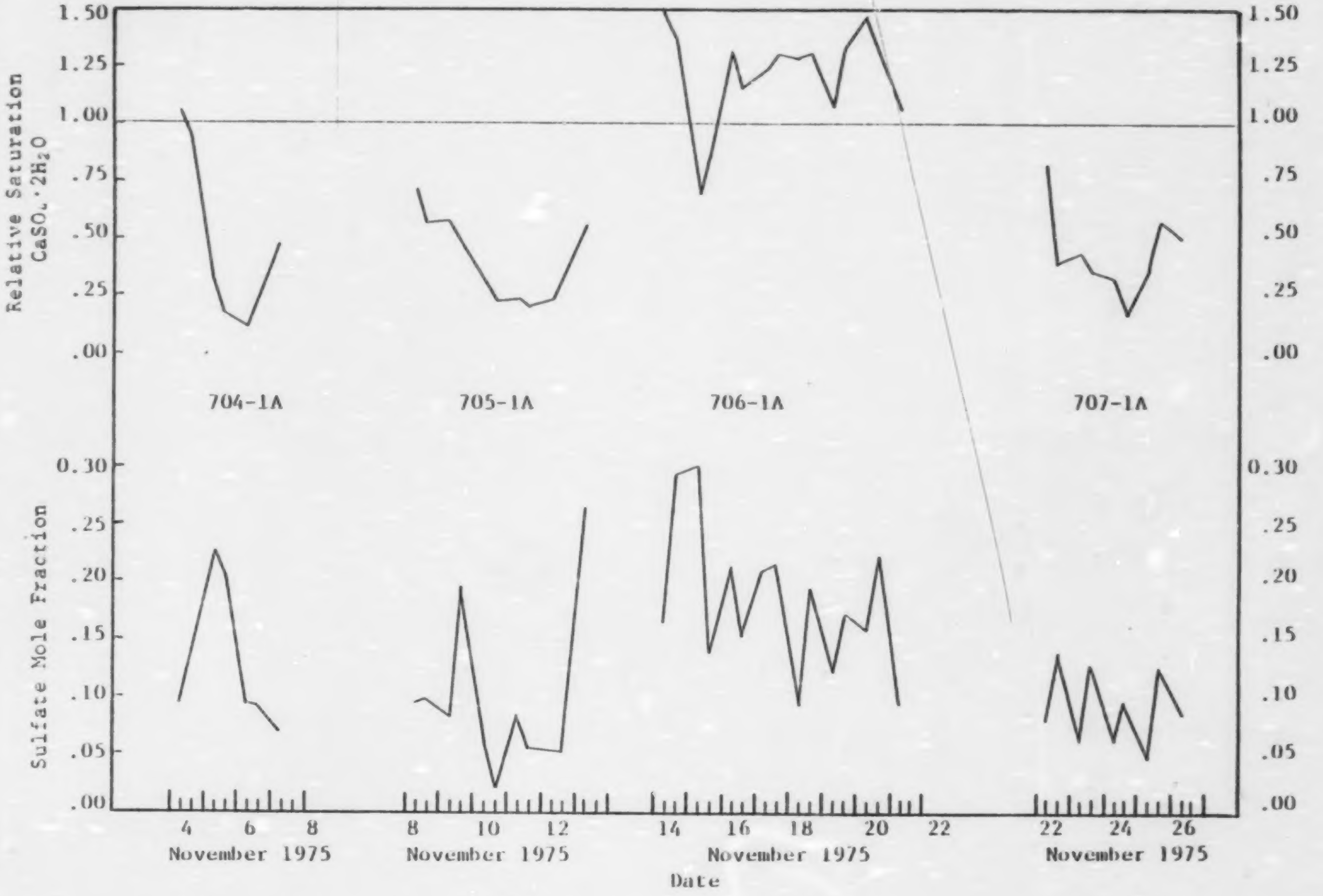

FIGURE B-14. RELATIONSHIP BETWEEN SULFATE MOLE FRACTION AND GYPSUM RELATIVE SATURATION FOR SHAWNEE VENTURI/SPRAY TOWER-LIME RUNS

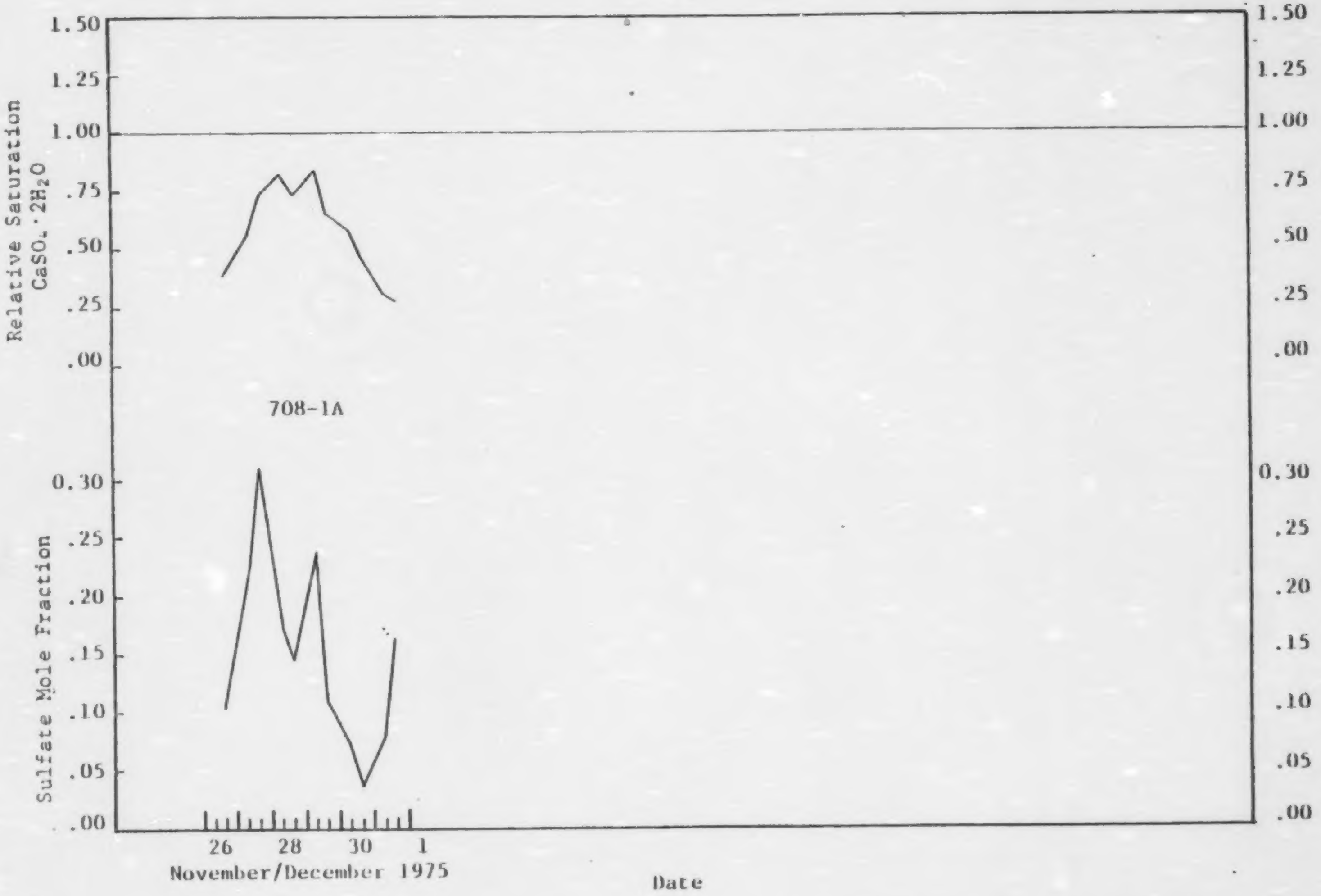

FIGURE B-15. RELATIONSHIP BETWEEN SULFATE MOLE FRACTION AND GYPSUM RELATIVE SATURATION FOR SHAWNEE VENTURI/SPRAY TOWER-LIME RUNS

An examination of the data in Figures B-2 through B-15 shows that there were never periods of reasonably constant relative saturation. Furthermore, there were several periods during which gypsum could be formed. The suitability of the Shawnee data for this particular correlation is somewhat doubtful.

In view of these considerations, analysis of the Shawnee data was limited to observation of general trends. Analysis of Figures B-10 to B-15 reveals that an increase in the relative saturation of calcium sulfate dihydrate was accompanied by an increase in the sulfate content of the solids (higher sulfate mole fraction). Also, a decrease in the relative saturation of calcium sulfate dihydrate was accompanied by a general decrease in the sulfate content of the solids.

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APPENDIX C

"EXPERIMENTAL EQUIPMENT AND SAMPLING TECHNIQUES"

Prepared by:
Larry A. Rohlack

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1.0 INTRODUCTION

The laboratory equipment used to fulfill the experimental segment of this program is described in this appendix. Experimental measurements were made to characterize those factors which influence the formation of the solid solution.

Three different types of experimental equipment were utilized during this program. They were:

- an early phase equilibrium apparatus,
- an equilibrium extraction apparatus, and
- a kinetics apparatus.

The early phase equilibrium apparatus was designed to establish whether a solid solution would precipitate from various solutions near equilibrium conditions. The equilibrium extraction apparatus was used to obtain equilibrium data from solids grown using the kinetics apparatus. A kinetics apparatus was set up to obtain quantitative measurements relating variables which influence the formation of the double salt. Along with the three types of experimental apparati, the sampling trains, sampling techniques, and operational procedures will be discussed in the remainder of this Appendix.

2.0 EARLY PHASE EQUILIBRIUM APPARATUS

The primary purpose of the early phase equilibrium apparatus was to grow calcium sulfite hemihydrate ($CaSO_3 \cdot \frac{1}{2}H_2O$) at conditions approaching equilibrium in order to establish whether a true solid solution would precipitate. Also a quantitative relationship between equilibrium liquid and solid phase composition was to be established using this equilibrium device.

A schematic diagram of this apparatus is shown in Figure 2-1. The primary components are:

- a constant temperature precipitation vessel,
- condenser and vacuum control system,
- constant head device,
- sulfite saturator, and
- sampling train.

2.1 Constant Temperature Precipitation Vessel

The primary purpose of the constant temperature vessel was to allow precipitation to occur at precisely controlled conditions. A 22-liter West-ef flask served as the precipitation vessel while a 22-liter heating mantle supplied heat to the liquor within the precipitation vessel. A thermistor was used to both monitor and maintain a constant temperature within the vessel. Liquor agitation within the precipitation vessel was accomplished by using a laboratory stirrer and a West-ef vacuum-tight stirring apparatus. Oxygen-free nitrogen gas was slowly bubbled just below

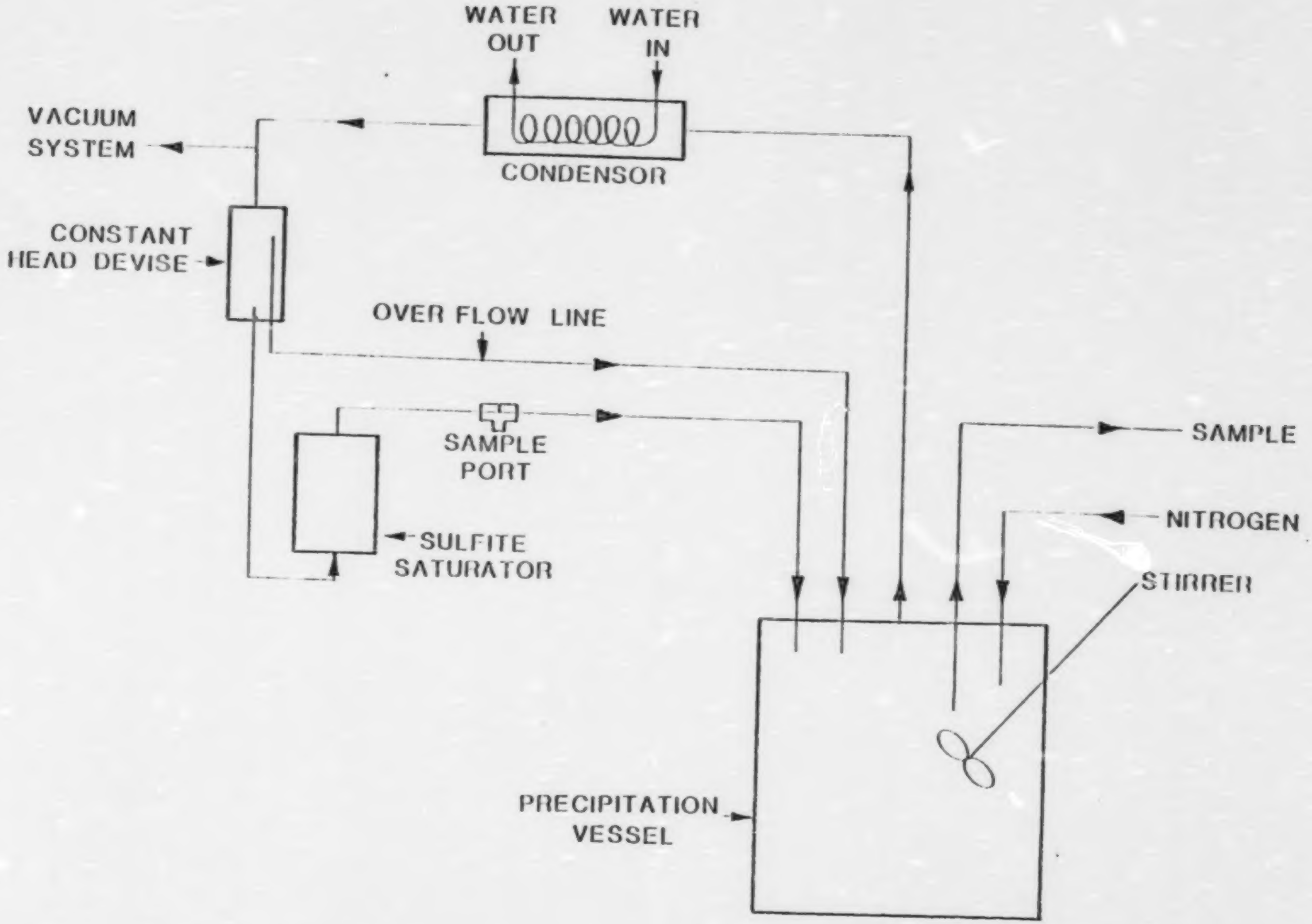
WATER OUT
WATER IN
VACUUM SYSTEM
CONDENSOR
CONSTANT HEAD DEVISE
OVER FLOW LINE
SAMPLE PORT
SAMPLE
NITROGEN
SULFITE SATURATOR
STIRRER
PRECIPITATION VESSEL

Figure 2-1 Schematic of Early Equilibrium Apparatus

the surface of the liquor in the precipitation vessel to minimize oxidation and to break up the surface tension and therefore equalize the evaporation rate.

2.2 Condenser

Water vapor leaving the precipitation vessel passed through a specially designed condenser. This condenser was designed and built at Radian because of the inability of commercially available condensers to work efficiently in this situation. Condensed water leaving the condenser passed through a West-ef right-angle glass joint. To the top of this joint, a vacuum line was attached and to the bottom a constant head device was attached.

2.3 Constant Vacuum System

The vacuum within the system was maintained at a constant value by using a vacuum pump, a mercury manometer, and a vacuum regulator/controller unit. By maintaining a constant vacuum in the system, a constant evaporation rate could be maintained.

2.4 Constant Head Device

Condensed liquor leaving the right-angle joint entered the constant head device. This device consisted of a thick-walled glass cylinder and a rubber stopper with two movable glass tubes in it. The center glass tube allowed liquor to flow to the sulfite saturator while the outside glass tube allowed liquor to flow directly to the precipitation vessel. By raising or lowering the outside tube, different pressure heads could be placed on the center glass tube thus varying the liquor flow to the sulfite saturator. Any liquor not passing through the center glass tube was channeled back to the precipitation vessel by means of the outside glass tube.

2.5 Sulfite Saturator

Water leaving the constant head device by means of the center glass tube entered at the bottom of the Plexiglas sulfite saturator. In the saturator, the liquor was thoroughly mixed with calcium sulfite hemihydrate crystals allowing the liquor to become saturated with calcium sulfite. The liquor then passed through a nuclepore polycarbonate filter in the top of the saturator in order to separate undissolved solids from the liquor. Gravity flow then forced the liquor back to the precipitation vessel.

2.6 Sampling Train

Two types of sampling trains were used during this segment of the program: a vacuum sampling train which was used during the run, and a pressure sampling train used after the completion of a run. Each sampling train was designed so that minimal changes in sample composition occurred during sampling and that sampling effects on the equilibrium of the system were kept to a minimum.

2.6.1 Vacuum Sampling

Two vacuum sampling trains were designed to sample the liquor in the precipitation vessel and the liquor leaving the saturator without having to bring the system to atmospheric or positive pressure.

A rather uncomplicated but effective sampling train was used in sampling the liquor leaving the saturator. A 500-ml Erlenmeyer flask fitted with a one-hole stopper served as the collection device. A vacuum greater than that in the precipitation vessel was pulled on the 500-ml Erlenmeyer flask. This flask was then attached to the line leading from the saturator to the precipitation device. The vacuum in the flask was allowed to equilibrate with the vacuum in the precipitation device causing saturator liquor to flow into the flask. After detaching the flask, nitrogen was used to equalize the pressure in the flask with that of the atmosphere. The liquid could then be analyzed or stored in the proper medium.

The second vacuum sampling train was used to sample the precipitation vessel liquor during a run. This sampling train consisted of a vacuum pump, a collection device, a filter and a teflon line. The vacuum pump was used to slowly pull liquor out of the precipitation vessel through a teflon tube suspended below the liquor level. Liquor leaving the precipitation vessel passed through a filter and was then collected in the collection device. After sufficient sample was collected, the collection device vacuum was equalized with nitrogen gas. The liquor could then be analyzed or stored in the proper medium.

2.6.2 Pressure Sampling

After the completion of a run, the solids in the precipitation vessel along with the final liquor samples were collected. This was accomplished by forcing oxygen-free nitrogen gas into the precipitation vessel which in turn forced the slurry out of the vessel by means of the teflon sampling line. The slurry then passed through a filter where the solids were separated from the liquor. A portion of the filtrate was collected for analysis of liquid phase cations and anions. After filtration of the precipitation vessel liquor was completed, nitrogen gas was used to purge the filter cake of excess water and to partially dry the solids. This final step minimized oxidation problems.

3.0 EQUILIBRIUM EXTRACTION APPARATUS

In order to differentiate between the equilibrium and kinetic effects on the sulfate content of solids grown under various kinetic conditions, an equilibrium extraction apparatus was designed and constructed. This apparatus was so designed that solids would be allowed to dissolve and reprecipitate very slowly in a liquor similar to the liquor in which the solids were grown. This slow dissolution/precipitation process should allow the kinetic effect(s) to be extracted from the equilibrium effect.

Primary components of the equilibrium extraction device (Figure 3-1) include:

- a Plexiglas box,
- the temperature control system,
- a mechanical tumbler,
- 570 ml plexiglas cylinder, and
- a sampling train.

3.1 Plexiglas Box

The primary purpose of the plexiglas box was to provide an enclosure in which the equilibrium apparatus could be maintained at a controlled temperature in an oxygen-free atmosphere.

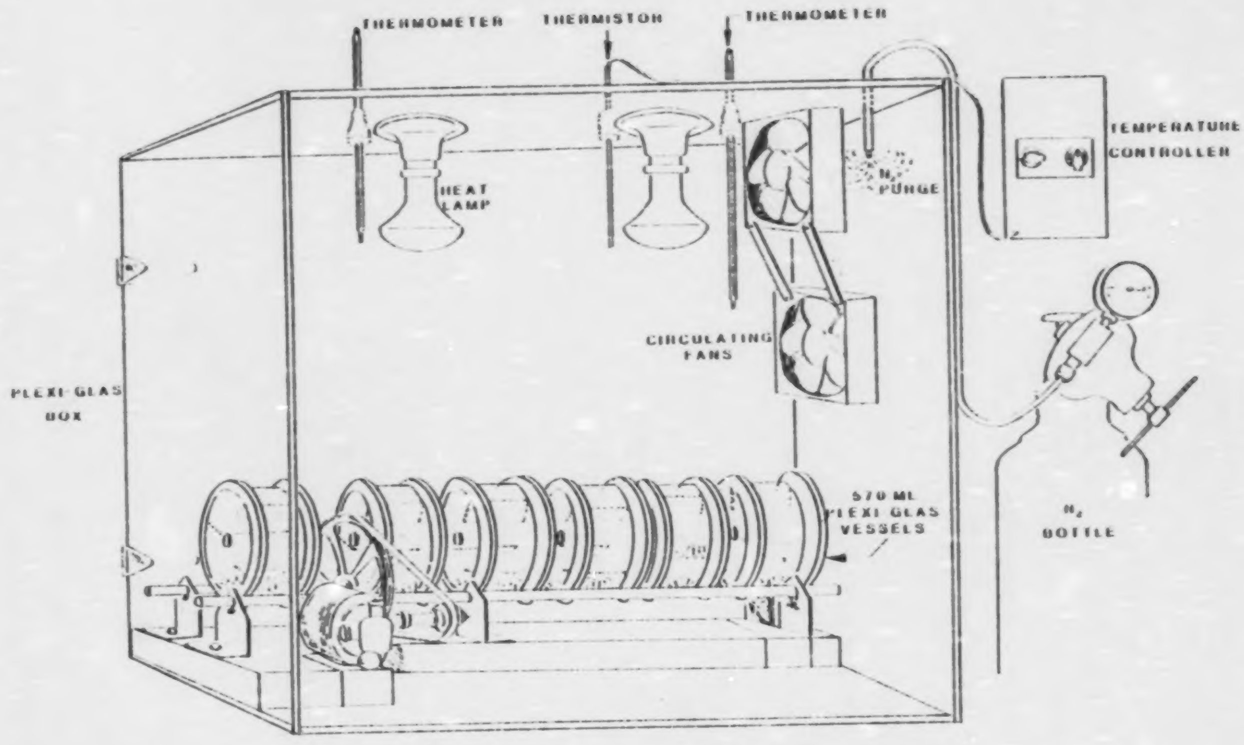
THERMOMETER
THERMISTOR
THERMOMETER
HEAT LAMP
N_2 PURGE
TEMPERATURE CONTROLLER
CIRCULATING FANS
PLEXI-GLAS BOX
570 ML PLEXI GLAS VESSELS
N_2 BOTTLE

Figure 3-1 Schematic of Equilibrium Extraction Apparatus

3.2 Temperature Control System

In order to simulate the conditions at which the solids were grown, the liquor temperature had to be maintained as close to the actual run temperature as possible during the equilibrium experiment. This was accomplished by using a temperature control system which is described in the following paragraph.

Two heat lamps suspended from the top of the plexiglas box provided an excess of radiant heat needed to maintain a temperature of $50^{\circ}C$ inside the enclosure. Two small circulating fans were used to circulate the nitrogen atmosphere within the enclosure ensuring that there were no temperature gradients within the plexiglas box. To ensure that there were no drastic temperature gradients within the enclosure, temperature measurements taken simultaneously at different points inside the box showed a temperature deviation of less than $1^{\circ}C$ at any two points in the box. A thermistor attached to a temperature controller maintained a constant temperature within the enclosure by cycling the heat lamps on and off. The temperature controller was able to maintain $50^{\circ}C$ at the thermistor within $\pm 0.4^{\circ}C$.

3.3 Mechanical Tumbler

The primary purpose of the mechanical tumbler was to provide a means of simultaneously rotating six sample vessels horizontally in order to mix the vessels' contents. The vessels were situated on two rotating shafts that were rotated by a variable speed motor which enabled the vessels to be rotated at rates as low as one revolution per minute. (Average vessel rotation speed was 4-5 revolutions per minute.) The entire tumbler arrangement was mounted on a stationary base and set inside the temperature controlled box.

3.4 570 ml Plexiglas Vessel

The plexiglas container served as a reaction vessel for the equilibration of the kinetic run solids with an appropriate liquor characteristic of their mother liquor. The containers were made of half-inch plexiglas and held 570 ml ± 5 ml. A threaded hole in the side of the plexiglas container was used for charging the containers with the appropriate slurry and also enabled samples to be taken from the vessel. Quarter-inch burundum cylinders were placed in the vessels to help mix the contents and enhance dissolution of reactor solids by grinding up the solids and thus exposing new surfaces to the liquor.

3.5 Sampling Train

The sampling train described in Figure 3-2 was designed so a representative sample of the filtered vessel liquor could be obtained without any undesirable changes in the actual sulfite and sulfate liquor or solid composition.

A pH meter utilizing a combination electrode was used to measure the pH of the liquor in situ, (as illustrated in Figure 3-2). A nitrogen blanket was kept directly above the vessel's sample port to minimize the chances of sulfite oxidation during pH measurement and aqueous sampling.

A peristaltic pump was used to transfer the liquor from the plexiglas vessel to the proper collection device for analysis or storage. Upon leaving the plexiglas vessel, the liquor passed through a 47 mm filter holder where the solids were separated from the liquor so any suspended solids would not interfere with the analysis of the liquor phase.

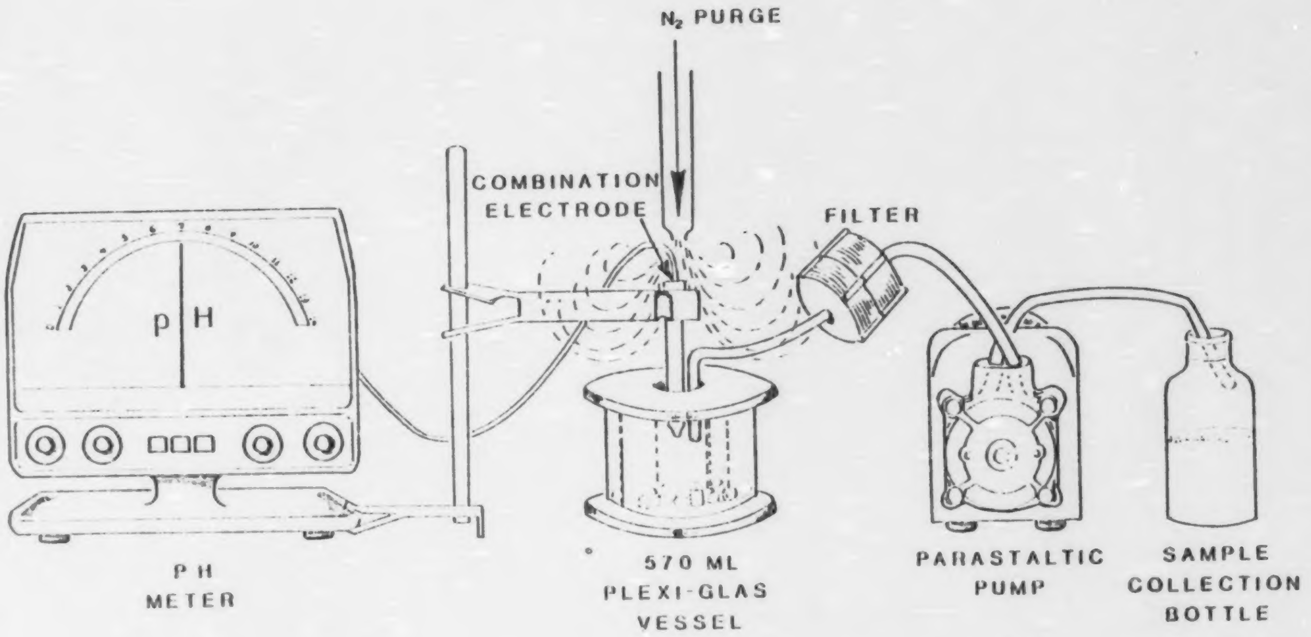
N2 PURGE
COMBINATION ELECTRODE
FILTER
p H
P H METER
570 ML PLEXI-GLAS VESSEL
PARASTALTIC PUMP
SAMPLE COLLECTION BOTTLE

Figure 3-2 Sampling Train for Equilibrium Extraction Apparatus

Nalgon or silicon tubing was used in the sampling train because of their chemical inertness to the species in question. Also, all sampling lines were kept as short as possible in order to minimize transit time.

A description of the samples and the sampling techniques used in obtaining solid and aqueous samples during this segment of the project are given in Table 3-1. All sampling and sample handling techniques used during this segment of the project were found to be consistent with the accurate measurement of both sulfite and sulfate in the solid and liquid samples.

TABLE 3-1

SAMPLE COLLECTION TECHNIQUES

Sample	Species in Question	Sampling Technique Used
Aqueous SO_2	$SO_3^=$ (Sulfite)	A known volume of aqueous sample is collected in a glass bottle containing a known volume of buffered standard iodine solution.
Diluted Filtrate	Total Sulfur, Calcium, Sodium, Magnesium, and Chloride	A known volume of aqueous sample is collected in a linear polyethylene bottle containing a known amount of water and hydrogen peroxide. The peroxide converts any sulfite to sulfate so no sulfur is lost to the atmosphere.
Solids in Vessel	Sulfite, Sulfate, and Calcium	The slurry remaining in the vessel after collection of aqueous samples is filtered under a nitrogen blanket using a nuclepore filter and a 47 mm millipore filter apparatus. Filtered solids are then rinsed with acetone to remove excess liquor. They are then dried at 40°C in an inert atmosphere.

4.0 EXPERIMENTAL APPARATUS UTILIZED IN THE KINETIC STUDIES

This kinetic apparatus served as a precipitation device from which quantitative measurements could be obtained for correlating variables which influence the formation of the double salt. With this apparatus, experimental conditions such as temperature, calcium sulfite precipitation rate, relative saturation of calcium sulfate, magnesium concentration, and ionic strength could all be varied independently to simulate the reactor compositions required by the scope of work in this program.

Topics discussed in the remainder of this Appendix are:

(1) description of equipment,

(2) sampling train,

(3) sampling techniques, and

(4) operational procedure.

4.1 Description of Equipment

This segment of Appendix C describes the various components which comprised the kinetics apparatus. This equipment was adequate in studying the precipitation of calcium sulfite hemihydrate at various conditions which favor the formation of the double salt.

A schematic diagram of this apparatus is shown in Figure 4-1. The essential components are:

(1) continuous liquor/slurry feed system,
(2) reactor,
(3) ball mill,
(4) continuous mixed product removal system, and
(5) pH monitor.

4.2 Continuous Liquid/Slurry Feed System

The continuous liquid/slurry feed system supplies the reactor with two well-defined feed streams. Parameters such as liquor composition, flow rate, and temperature can be varied and accurately controlled to study the effect these variables have on the mole fraction sulfate in the solids.

Two 60-liter linear polyethylene containers were used to mix and store the feed stream solutions. Whenever a slurry feed stream was used, a stirrer maintained a homogeneous mixture in the feed tank. Peristaltic pumps and controllers were used in transferring the feed streams from the feed tanks to the reactor at accurately controlled flow rates. Because the feed stream liquor density usually changed from run to run, a rotameter was used to monitor the flow rate of the feed streams. Before entering the reactor, the feed streams passed through a constant temperature water bath so the reactor temperature could be varied as desired from 30°C to 60°C. Upon leaving the constant temperature bath the feed streams passed through a three-way stopcock. At this point the feed streams could be diverted from the reactor to the feed stream sampling points.

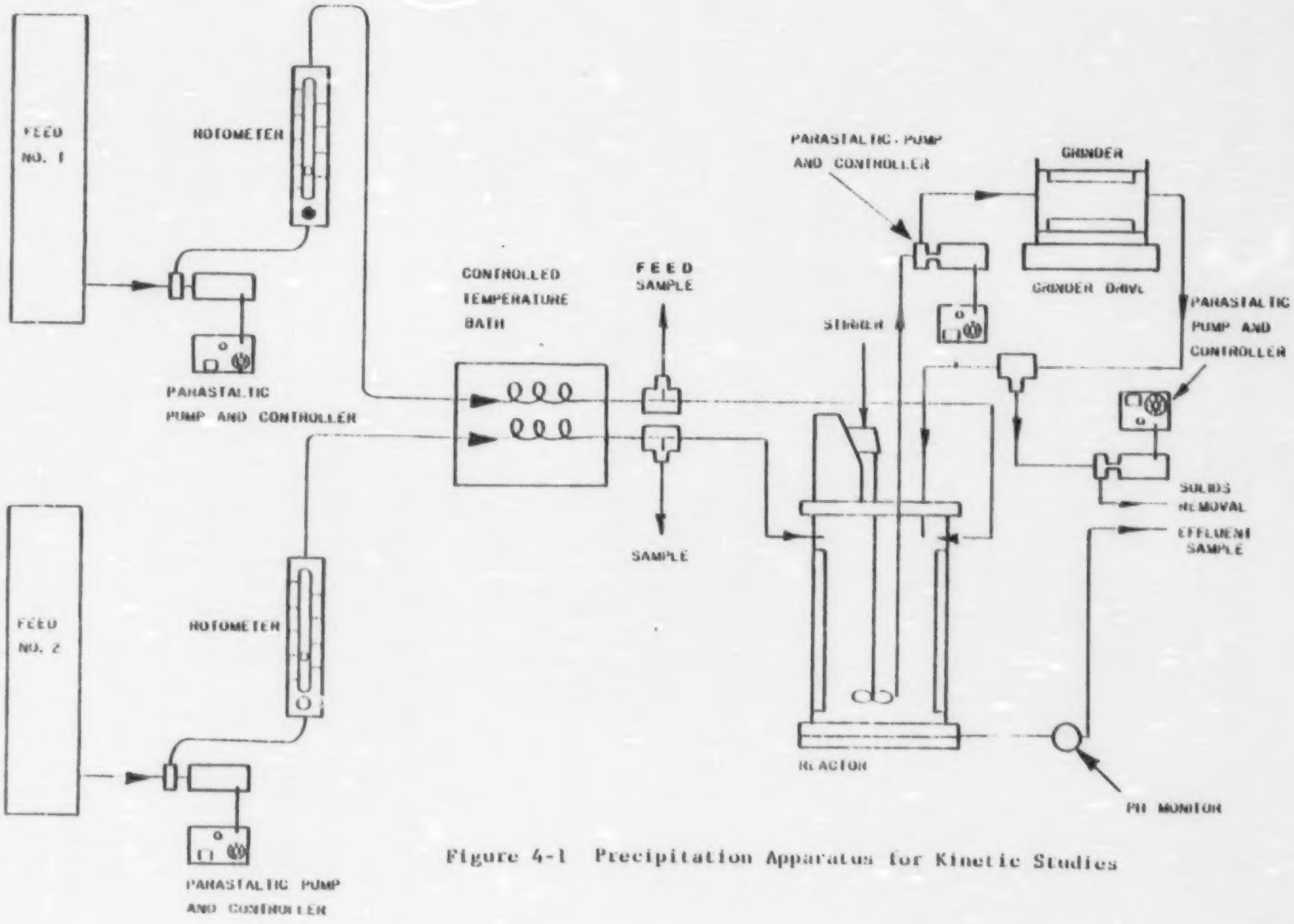
FEED NO. 1
ROTOMETER
PARASTALTIC PUMP AND CONTROLLER
FEED NO. 2
ROTOMETER
PARASTALTIC PUMP AND CONTROLLER
CONTROLLED TEMPERATURE BATH
FEED SAMPLE
SAMPLE
PARASTALTIC PUMP AND CONTROLLER
GRINDER
GRINDER DRIVE
PARASTALTIC PUMP AND CONTROLLER
STIRRER
SOLIDS REMOVAL
EFFLUENT SAMPLE
REACTOR
PH MONITOR

Figure 4-1 Precipitation Apparatus for Kinetic Studies

4.3 Reactor

A specially designed 2750 ml plexiglas reactor, as described in Figure 4-2, served as a reaction vessel for the mixing of the feed streams and the precipitation of the calcium sulfite-sulfate double salt.

The feed streams were input to the reactor at angles of 180 degrees to each other and directed toward a propeller to insure minimum mixing time of the feed streams. A second propeller near the bottom of the reactor suspended the solids while baffles broke up the circular motion of the liquor and enhanced mixing. Oxygen-free nitrogen gas could be forced into the top of the reactor to either purge the system of oxygen or force liquor from the reactor. The reactor liquor temperature was monitored by a thermometer mounted in a hole in the top of the reactor. A 142 mm diameter nuclepore filter in the bottom of the reactor was used to separate the solids from the liquor to obtain a clear effluent for pH monitoring and chemical analysis.

Two of the factors affecting the calcium sulfite precipitation rate are the number and particle size of the calcium sulfite seed crystals. It was desirable in the kinetic studies to maintain a constant precipitation rate during an experimental run and during a series of experimental runs. A ball mill (Figure 4-3) was designed and built especially for use with the kinetics apparatus to maintain a constant particle size at a fixed slurry removal rate during a run. This facilitated the accurate assessment of kinetic influences of the calcium sulfite precipitation rate.

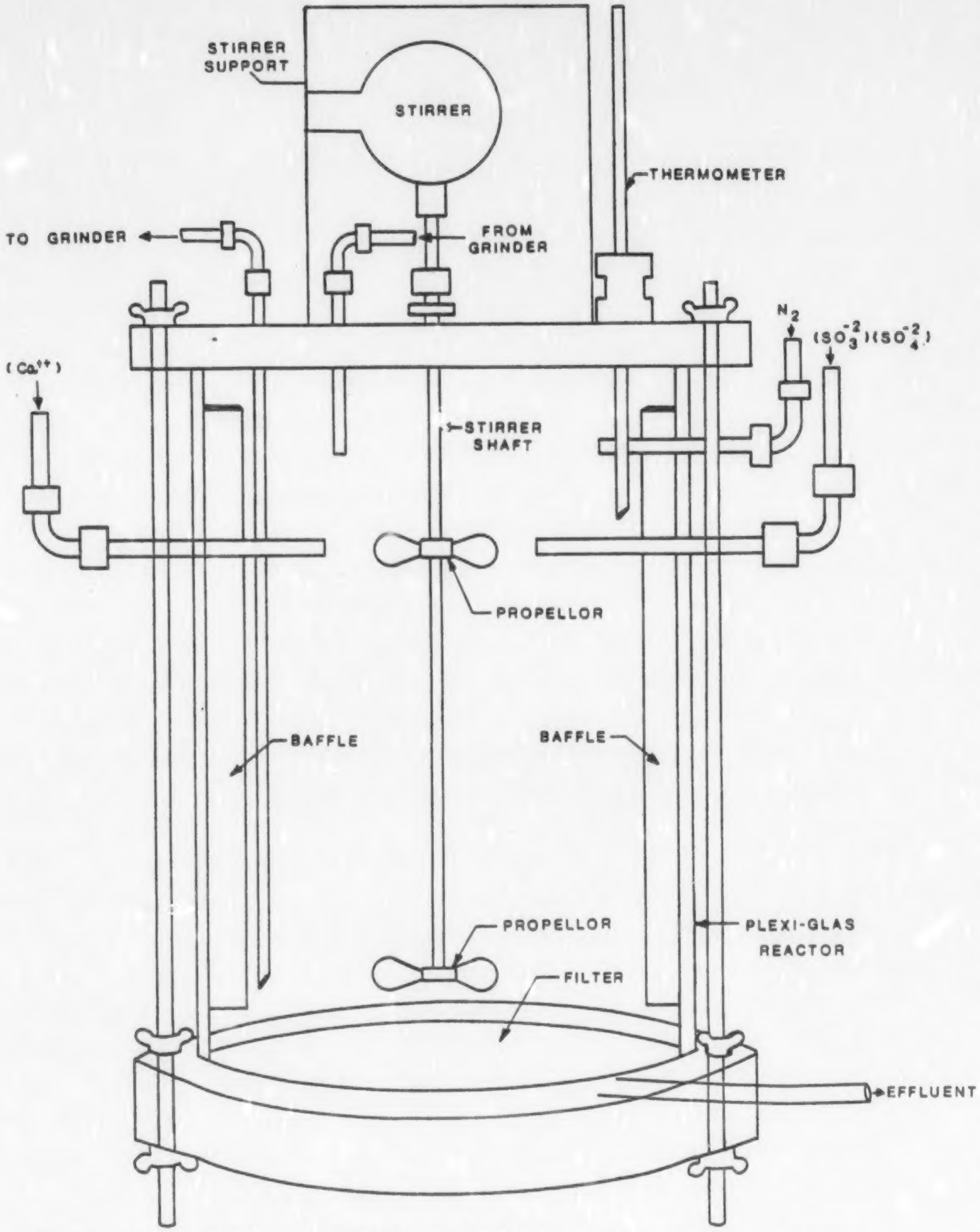
STIRRER SUPPORT
STIRRER
THERMOMETER
TO GRINDER
FROM GRINDER
N_2
$(SO_3^{-2})(SO_4^{-2})$
(Ca^{++})
STIRRER SHAFT
PROPELLOR
BAFFLE
BAFFLE
PROPELLOR
PLEXI-GLAS REACTOR
FILTER
EFFLUENT

FIGURE 4.2. PLEXI-GLAS REACTOR USED IN THE KINETIC STUDIES

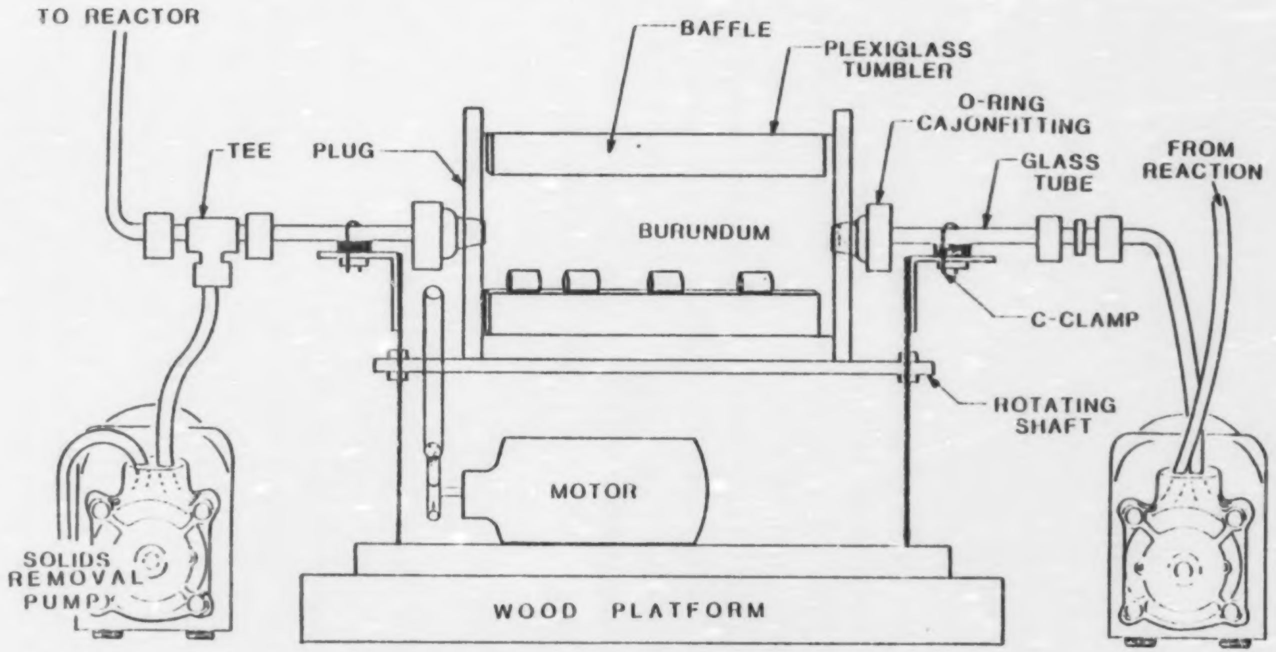
TO REACTOR
TEE
PLUG
BAFFLE
PLEXIGLASS TUMBLER
O-RING CAJONFITTING
GLASS TUBE
FROM REACTION
BURUNDUM
C-CLAMP
ROTATING SHAFT
MOTOR
SOLIDS REMOVAL PUMP
WOOD PLATFORM

Figure 4-3. BALL MILL

4.4 Ball Mill

The primary components of the ball mill are a 500 ml plexiglas cylinder, a tumbling device, a peristaltic pump, and transfer lines as illustrated in Figure 4-3. Materials used to build the ball mill were chosen because of chemical inertness and ability to be fabricated.

The primary purpose of the plexiglas vessel was to provide an enclosure in which the reactor slurry could be placed and rotated. Burundum cylinders (1/4-inch outside diameter) were placed inside the plexiglas vessel with the sole purpose of grinding up particles passing through the ball mill. Baffles were installed in the plexiglas vessel to keep the contents homogeneous and to provide a mechanism by which the burundum cylinders could ride partially up the wall of the plexiglas vessel and then fall to the bottom to grind particles. Threaded holes on either side of the vessel allowed Cajon fittings to be attached to the vessel.

The Cajon fittings in either end of the plexiglas vessel enabled the vessel to rotate without rotating the glass inlet and outlet tubes. The remainder of the tumbling device was comprised of two shafts, a motor, and a means of support. The plexiglas vessel sat on the two rotating shafts. A small variable speed motor and pulley arrangement enabled the two shafts and thus the vessel to be rotated at a controlled rate from 10 to 100 revolutions per minute. Most runs were made with a rotational speed of 25 to 50 revolutions per minute depending on run time and precipitation rates.

A peristaltic pump was used to draw reactor slurry from the bottom of the reactor (refer to Figure 4-1) to the plexiglas vessel. This continuous transfer of slurry from the reactor caused slurry to flow through the ball mill allowing grinding to occur. Slurry leaving the ball mill passed first through a one-fourth inch glass tube, then a teflon tee, and then re-entered the reactor at the top (again refer to Figure 4-1). All transfer lines were of glass or silicone tubing due to their chemical inertness to the species in question.

4.5 Continuous Mixed Product Removal System

Because the number of particles present in a system at any one time affects the precipitation rate, a means of maintaining a constant number of particles in the reactor had to be developed. A continuous mixed product removal system was incorporated into the kientics apparatus so the number of particles in the reactor would remain constant during a run. The primary components of this system are a teflon tee, a peristaltic pump, and a time sequence unit.

Slurry leaving the ball mill passed through a teflon tee where a slipstream was removed from the system by means of a peristaltic pump. At a constant particle size, temperature, and driving force the precipitation rate would be held at a desirable level by maintaining a constant slurry density. Slurry density could be controlled by the flow rate of the slip stream.

The slurry removal pump had a capacity range of 10-150 ml slurry/min. If the calculated flow rate needed to maintain a certain solids content was less than 50 ml per minute, a time sequence unit was used to cycle the peristaltic pump off and on. The peristaltic pump's flow rate would be set at 50 ml per minute and then the time sequence unit would be adjusted to be on for a specified time and then off for a specified time resulting in the desired removal rate. Periodic removal at a higher flow rate was used to ensure that representative slurry was removed.

4.6 pH Monitor

Effluent leaving the bottom of the reactor passed through a 100 ml three-necked flask where the pH of the solution was monitored. Inlet and outlet lines and thermometer were situated in the center port of the flask, while the two pH electrodes were situated in the other ports. Because of the small volume the residence time was kept short, thus minimizing the possibility of change in solution composition. Effluent leaving the pH monitor was collected periodically during a run for analysis.

5.0 SAMPLING TECHNIQUES

Sampling and sample handling techniques developed for use during this segment of the program were made to be consistent with accurate measurements of sulfite and sulfate in both liquid and solid phases. Sampling techniques used during this segment of the program can be found in Table 5-1.

Collection of Solids in the Presence of $MgSO_4$

One of the difficult problems in characterizing the solids precipitated from these solutions is the contamination of the solids by high liquid phase magnesium sulfate. This contamination results from the adhesion of the liquid phase to the filtered solids with subsequent crystallization of the magnesium sulfate during drying. Therefore, every possible precaution must be taken to ensure minimal reactor liquid contact with the solids after filtration.

The procedure which was developed to remove reactor liquor from filtered solids consisted primarily of washing the solids several times under a nitrogen blanket with saturated calcium sulfite liquor. A saturated solution of calcium sulfite was prepared by dissolving calcium sulfite solids in oxygen free deionized water. After the solids from a run containing high $MgSO_4$ were filtered, about 50 to 100 ml of the saturated calcium sulfite liquor was added to the solids to form a slurry. This slurry was then filtered and the washing step repeated. After three or four calcium sulfite washings, several acetone washings were performed. All of these washings and filterings were performed under a nitrogen blanket to minimize any oxidation of sulfite to sulfate. The final washed solids were placed in a nitrogen-purged oven set at 40 to 45°C for final drying.

TABLE 5-1

SAMPLE COLLECTION TECHNIQUES

Sample	Location	Technique Used
Aqueous SO_2	Sulfite Feed and Effluent	Sample collected in a glass bottle containing a buffered iodine solution.
Diluted Filtrate	Limestone Feed	Sample collected in a linear polyethylene bottle containing a known amount of hydrochloric acid.
Diluted Filtrate	Calcium Feed (clear liquor)	Sample collected in a linear polyethylene bottle containing a known amount of water.
Diluted Filtrate	Sulfite Feed and Effluent	Sample collected in a linear polyethylene bottle containing a known amount of water and hydrogen peroxide.
Aqueous CO_2	Effluent	Effluent collected in a linear polyethylene bottle containing 5 ml of CO_2 buffer.
Weight % Solids	Exit Side of Solids Removal Pump	100 milliliters of reactor slurry was collected in a volumetric flask, slurry was then filtered using a 47 millimeter millipore apparatus.
Reactor Solids	Exit Side of Solids Removal Pump	Reactor slurry is forced through a nuclepore polycarbonate filter held in a 147 millimeter millipore filter apparatus. Excess liquor is separated from solids by forcing nitrogen through the polycarbonate filter.
Reactor Solids in Presence of High Magnesium Concentrations	Exit Side of Solids Removal Pump	Same as reactor solids above except these solids are thoroughly washed with a saturated sulfite solution to remove any liquid phase magnesium sulfate.

Upon analyzing the washed and dried solids there were negligible amounts of magnesium found in the solids, thus verifying the effectiveness of this procedure. The amount of magnesium found in the solids represented a positive error in the sulfate analysis of less than 1%.

6.0 OPERATIONAL PROCEDURE

In this section of Appendix C the operational procedure used in performing kinetics runs shall be discussed. All of the operational procedures used during this segment of the program were developed to minimize undesirable changes in either the solid or liquid phases within the feed tanks, transfer lines, or reactor. Steps were also taken to ensure maximum ease of operation during the kinetics run, thus enabling the operator to concentrate on the progress of the experimental run and ensuring the collection of more viable data. For a given set of operating conditions, the following operational procedures were developed to fulfill the objectives of the run.

Initially, the temperature bath was turned on and the proper temperature setting selected. Then the two feed tanks were thoroughly cleaned and filled with the appropriate quantity of deionized water. In order to minimize oxidation during a run, oxygen-free nitrogen gas was bubbled through the feed tanks, thus purging any dissolved oxygen from the deionized water and forming a blanket of inert nitrogen gas above the water. This protective blanket of nitrogen gas was maintained as the liquid level decreased during the run.

During the purging by nitrogen gas, there was sufficient time to thoroughly clean the reactor and grinder. All foreign material was removed by first rinsing the reactor and grinder with a dilute HCl solution which helped loosen and dissolve any scale which may have formed during the previous run. After sufficient HCl solution had been rinsed through both grinder and reactor, a sufficient amount of deionized water was used to finish cleaning the reactor and grinder. After rinsing, the reactor and grinder were examined for physical abnormalities which were corrected before final assembly of the two units. Oxygen-free nitrogen gas was used to purge any oxygen in the reactor and grinder prior to the run. After final inspection of the reactor and grinder the proper quantities of chemicals were added to the already purged feed tanks. Then, depending on the amount of agitation required to completely dissolve the chemicals in the feed tanks, either manual stirring or a laboratory stirrer was used to agitate the liquor. Whenever a slurry feed stream was used, a laboratory stirrer was used to maintain a homogeneous solution throughout the course of the run. A flotation lid was used whenever possible to minimize liquid-air contact and a plexiglas lid was kept on top of the feed tanks at all times in order to keep out foreign particles and also minimize any air turbulence above the flotation lid.

After the feed tanks were properly prepared and the reactor and grinder were ready for use, feed stream flow rates were then ready to be set and feed stream samples were ready to be taken. The peristaltic pumps used to control the flow rates of the two feed streams were turned on and flow was diverted to the sample ports. Rotameters gave a visual indication as to the amount of flow occurring and were used to maintain a constant flow throughout the course of a run. By adjusting the peristaltic pump controller, the flow rate as indicated by rotameter could be set to a desired level. This flow rate was then verified by measurement with volumetric flask and stopwatch. After verification, feed stream samples were collected in the proper collection medium for analysis or storage.

Next, the feed stream flows were diverted back into the reactor at which time the reactor was allowed to fill with the two feed streams. The reactor stirrer was turned on and a stirring rate set by adjusting the voltage with a Variac. For the majority of the runs the stirring rate was maximum allowing for optimum agitation of reactor contents. While the reactor was filling, the seed crystals to be used for that particular run were added through the thermometer port and immediately mixed by the stirrer. Seed crystals were generally added at the start of reactor fill up in order to prevent homogeneous nucleation from occurring, thus increasing the amount of seed crystals and possibly changing the seed crystal composition. After the seed crystals were added, the thermometer was positioned and any nitrogen escaping the reactor during fill up passed through the loosened stirrer fitting. While the reactor was filling the peristaltic pump that controlled flow through the grinder was turned on and the grinder was filled with reactor slurry. After the grinder had been filled with slurry, the Variac controlling the grinder rotation speed was adjusted in order to obtain the desired revolutions per minute. The grinder speed used for most of the runs ranged from 25 to 50 rovolutions per minute with the grinder speed being dependent on the type of run and the run time. As soon as the reactor and grinder were filled with the liquor, the stirrer fitting was tightened down and liquid was forced through the filter membrane in the bottom of the reactor. At this time the timer was started and the run officially began. Liquor leaving the reactor was forced through a 100 milliliter pH monitor where two buffered pH electrodes were used to monitor the pH of the effluent. Liquor leaving the pH monitor could either be collected for analysis or discarded to waste.

As soon as an approximate precipitation rate could be calculated (usually within 30 to 40 minutes into the run), a solids removal rate could be set in order to maintain a constant number of crystals in the reactor. Therefore, about 15 minutes into the run an effluent sulfite sample was taken and an outlet sulfite concentration obtained from which a precipitation rate was calculated. At approximately the same time a solids content sample was taken and a solids density value obtained. From these two values a slurry removal rate was calculated and the peristaltic pump attached to the outlet of the grinder was turned on and set at a rate equivalent to the slurry removal rate. The slurry removal rate used during the majority of the runs ranged from 10 to 100 milliliters per minute. Whenever the solids removal rate was less than 50 milliliters per minute, the peristaltic pump controller was plugged into a sequential timer. This enabled the peristaltic pump to be pumping slurry at a faster rate than required, but because of the cycle time of the sequential timer the required solids removal rate could be achieved.

In order to characterize the precipitated solids with any degree of accuracy, it is necessary to minimize the fraction of the seed crystals found in the solids collected at the end of the run. This was accomplished by removing solids at a rate equal to the precipitation rate for a period of time equal to three residence times of the solids. This reduces the original seed contribution to less than 5%.

Sulfite feed stream samples were taken at the start and end of a run if the run time was two to three hours. But, if more time was required to make the run, sulfite feed stream samples were also taken during the middle of the run to monitor any oxidation which might have occurred. The feed stream supplying calcium to the reactor was usually only sampled at the end of the run because of the stability of the feed stream.

Effluent sulfite samples were collected to monitor approach to steady state and to monitor precipitation rate. Feed stream and effluent diluted filtrate samples were usually only taken at the end of the run with duplicate samples being taken of the effluent to ensure representative data.

Throughout the course of a run several parameters were monitored in order to ensure that the run conditions remained constant during the run. Feed stream flow rates were closely monitored by visual observation of the rotameter setting and by monitoring the total effluent flow rate. By controlling the feed stream flow rates, accurate precipitation rates could be determined and reactor conditions could be controlled throughout the course of a run. Feed stream flow rates were very stable with any fluctuations being easily and quickly readjusted with the peristaltic pump. The temperature of the water bath was monitored quite frequently during a run to ensure proper heating of the feed streams. Temperature fluctuations in the water bath were not noticeable as long as the feed stream flow rates remained constant. Slurry removal flow rates were very stable throughout the course of a run, yet slurry removal samples were taken every half hour to an hour to confirm the flow rate stability and to determine the concentration of the solids. The grinder revolving rate was stable within the limitations of the apparatus as long as the inlet and outlet glass tubes did not become misaligned.

APPENDIX D

"ANALYTICAL TECHNIQUES UTILIZED IN EXPERIMENTAL STUDIES OF SOLID SOLUTION FORMATION"

Prepared by:
Benjamin F. Jones
Donnie L. Heinrich

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1.0 INTRODUCTION

The analytical techniques documented in this technical note were utilized in determining the solid and liquid phase composition for the equilibrium and kinetic experimental studies of EPA Contract 68-02-1883. Significant analytical developments within this contract include modifications of the solid and liquid sulfite analyses and the development of a technique for the specific determination of the sulfate concentration in solids in the presence of large excesses of calcium sulfite. These procedures allow the accurate measurement of sulfite and sulfate in both the liquid and solid phases.

Characterization of the liquid phase consisted of pH, temperature, calcium, magnesium, sodium, chloride, carbonate, sulfite and sulfate measurements. Quantitative analysis of the solids included the determination of calcium, magnesium, sodium, carbonate, total sulfur, sulfite and sulfate concentrations. Qualitative identification and characterization of the coprecipitation product was made with X-ray diffraction and infrared techniques.

2.0 LIQUOR ANALYSIS

Chemical analysis of the liquid phase of the equilibrium and kinetic experimental studies consisted of quantitative measurement of the calcium, magnesium, sodium, chloride, carbonate, sulfite and total sulfur ions. These procedures are documented in the following sections.

Analytical results of these determinations are utilized along with pH and temperature measurements as inputs into Radian's aqueous chemical equilibrium program. The program calculates the activities of the ions and ion pairs and the relative saturation of key species such as calcium sulfate dihydrate and calcium sulfite hemihydrate. These calculations will be used with solid phase analyses to interpret the influence of liquid phase composition on the solid solution formation.

2.1 Calcium, Magnesium, and Sodium

Total calcium, magnesium, and sodium present in the liquid phase of the equilibrium and kinetic studies were determined by chemical analysis of the diluted filtrate sample utilizing atomic absorption spectroscopy.

Instrument

All absorbance measurements were made with the Perkin-Elmer Model 503 atomic absorption spectrophotometer. Operational instructions, provided with the instrument, were followed for the work.

The absorbance measurements, accrued internally, were illuminated on a four-digit readout and recorded manually. The output was also recorded directly using a strip-chart recorder.

Hollow cathode tubes provided the radiation source for the absorption process. Single element lamps were used for each of the ions tested.

Laboratory Equipment

(1) Atomic Absorption Spectrophotometer

(2) Hollow Cathode Tubes: Sodium, Calcium, and Magnesium

(3) Air: A clean dry air supply capable of maintaining 50 psi at a 55 liters/min. flow rate.

(4) Fuel: Acetylene

(5) Glassware:

a. 1 ml pipette
b. 2 ml pipette
c. 3 ml pipette
d. 4 ml pipette
e. 5 ml pipette
f. 10 ml pipette
g. 25 ml pipette
h. 50 ml pipette
i. 100 ml pipette
j. 50 ml volumetric flasks
k. 100 ml volumetric flasks

Reagents

(1) Calcium - 1000 mg/ℓ Fisher certified atomic absorption reference solution.

(2) Magnesium - 1000 mg/ℓ Fisher certified atomic absorption reference solution.

(3) Sodium - 1000 mg/ℓ Fisher certified atomic absorption reference solution.

(4) Hydrochloric acid

(5) Lanthanum chloride hexahydrate

Interferences

The analysis of the liquor samples for calcium, magnesium and sodium from the equilibrium and kinetic studies are carried out in the presence of a number of other ions which occur concurrently in the system. Sample aliquots are diluted in a 1% lanthanum solution to suppress known interferences. The effectiveness of this solution has been documented in Radian Technical Note 200-006-20.

Procedure

Preparation of Lanthanum Chloride Solution (1% Lanthanum, 5% HCl)

Transfer 50.8 g $LaCl_3 \cdot 6H_2O$ or 35.3 g $LaCl_3$ (anhydrous) to a 2-liter volumetric flask, add 200-300 ml deionized water and then add 100 ml concentrated HCl. After the $LaCl_3$ has dissolved, bring to volume with deionized water and store in a polyethylene bottle.

Calculation

The calculations were performed using a linear least squares regression on the standards to obtain a calibration curve from which the concentrations of the samples could be determined utilizing the following equation:

$$\text{mg/liter} = \frac{(a + bx)(DV)(DF)}{A}$$

and,

$$\text{mmoles/liter} = \text{mg/liter} \div AW$$

where,

a = intercept
b = slope
x = absorbance
DV = dilution volume (milliliters)
DF = dilution factor during sampling
A = aliquot size (milliliters)
AW = atomic weight

Preparation of Standards

The standards are prepared by diluting the certified 1000 ppm atomic adsorption reference solution to obtain concentrations in the optimum working range of the atomic absorption spectrometer. The standards are prepared with each new solution of 1% lanthanum.

(1) Calcium - 4 mg/ℓ and 2 mg/ℓ standard solutions are prepared from the reference standard (1000 mg/ℓ)

(2) Magnesium - .4 mg/ℓ and .2 mg/ℓ standard solutions are prepared from the reference standard (1000 mg/ℓ)

(3) Sodium - 1 mg/ℓ and .5 mg/ℓ standard solutions are prepared from the reference standard (1000 mg/ℓ)

Preparation of Samples

The samples should be diluted within the following ranges for optimum sensitivity.

(1) Calcium - 1-4 mg/ℓ
(2) Magnesium - .1-.4 mg/ℓ
(3) Sodium - .2-1 mg/ℓ

If necessary, two step dilution may be made, the first in deionized water and the second in the lanthanum chloride solution. The accuracy for each of these analyses within the range indicated is ±1%.

2.2 Sulfite

Sulfite in the liquid phase of the equilibrium and kinetic studies was determined by an iodometric titration with sodium arsenite as the titrant. The iodometric method employed in this project is a modification of the standard iodine oxidation of sulfite ions designed to avoid interferences from nitrite which may be present in solutions from lime/limestone scrubbing processes. The accuracy of the procedure at the 95% confidence level is ±2% over the range of .001-.100 moles/ℓ SO_3^{-2}. Utilizing a microburette, the method can be extended to .0001 moles SO_3^{-2}/ℓ with an accuracy of ±4% at the 95% confidence level.

The sample is added to an excess of buffered iodine solution. The iodine remaining after the stoichiometric oxidation of sulfite is titrated with standard sodium arsenite solution. An amperometric dead-stop method is used for the end-point detection.

The iodine solution is buffered to a pH of 6.0-6.2 to inhibit sulfite-nitrite and nitrite-iodine reactions. This also inhibits the hydrolysis of the iodine and enhances the complete reaction of sodium arsenite and iodine. Arsenite solutions give more accurate results than thiosulfate solutions in the presence of nitrite and are also more stable under ordinary conditions. The dead-stop end-point detection method gives more reliable and accurate results than starch indicators. In practice, the dead-stop method is also convenient and simple.

Equipment

(1) 50 ml buret, 10 ml microburette

(2) magnetic stirrer

(3) pipets (including 2 ml and 10 ml sizes); bulb pipet fillers; and 100 ml graduated cylinder

(4) 150 ml beakers (preferably graduated)

(5) four-ounce small mouth glass bottles

(6) microammeter apparatus:

  (a) two 1-cm square platinum-sheet electrodes mounted about 1 cm apart

  (b) 1.5 volt dry cell battery (a #735 "hobby" battery works well)

  (c) electrometer or microammeter, 0-25 μ amp

  (d) voltage divider

Reagents and Solutions

D.I. water and reagent grade chemicals should be used for all solutions.

1. Sodium Arsenite Stock Solution (∿ 0.010 mole/ℓ)

Dissolve 1.3 grams of $NaAsO_2$ into one liter of D.I. water. Standardize this solution using reagent grade 0.1 N standard iodine.

$$(\text{molarity of } NaAsO_2) = \frac{(\text{ml } I_2)\ (\text{normality of } I_2)}{2\ (\text{ml } NaAsO_2)}$$

2. Preparation of ∿ 0.1 Normal Iodine Solution

Dissolve 25 grams of potassium iodide (KI) in as little D.I. water as possible. Weigh accurately 12.69 grams of resublimed iodine and dissolve it completely in the saturated potassium iodide solution. When the dissolution of the iodine is completed, dilute with D.I. water accurately to one liter. A larger solution can be made up at one time, if desired. Iodine should be kept in a well stoppered, dark colored bottle, in a cool place. It need not be standardized if only used for the sulfite analysis since a blank is also run.

3. pH 6 Buffer

This solution contains 1 mole/ℓ NaAc and 0.05 mole/ℓ HAc. Pipet 2.9 ml of glacial acetic acid into 500 ml of D.I. water. Stir in 82 grams of NaAc and when completely dissolved make up to one liter. It is convenient to prepare several liters of this solution at a time since 50 ml is used for each analysis.

Procedure for Aqueous SO_2 Determination

The sample should be taken into a tared 250 ml bottle containing the iodine and buffer solution.

(1) Pour the buffered excess iodine sample bottle contents into a well washed 150 ml beaker containing a magnetic stirring bar. Rinse the sample bottle well with buffer and add the rinse to the beaker.

(2) Place the platinum electrodes in the solution, stir and connect the micro-ammeter. The current should be 15-24 microamps.

(3) Begin the titration with the .01 mole/ℓ sodium arsenite solution using the 50 ml buret. The color of the solution serves as a rough indicator of the state of the titration. The iodine color (red) changes to yellow 5 ml before the endpoint is reached. When the solution turns light yellow, the titration should be carried out drop-wise. The solution will become colorless one to two drops before the endpoint. The titration is completed when the current reaches 3-4 microamp.

(4) After the titration is completed, record the ml of sodium arsenite used and rinse the electrodes with D.I. water after removing them from the solution.

(5) Blanks are to be run each day using the above procedure without the addition of the sample.

Calculations

The concentration of total SO_2 in the sample can be calculated using the following equation.

$$C = \frac{(B-S)M}{W_2-W_1}$$

where,

C = concentration of total SO_2 (mole/liter)

B = volume of arsenite solution needed to titrate the blank (ml)

S = volume of arsenite solution needed to titrate the sample (ml)

M = molarity of the arsenite solution, mole/liter (usually 0.0100)

W_1 = weight of bottle plus fixing solution (grams)

W_2 = weight of bottle plus fixing solution plus sample (grams)

2.3 Sulfate

Total sulfate present in the liquid phase of the equilibrium and kinetic studies was determined by indirectly measuring the total sulfur concentraton and subtracting the aqueous sulfite concentration. This section will discuss the method used in the analysis for total sulfur.

The aqueous sulfite is converted to the sulfate ion by oxidation of the liquor with a two-fold excess of H_2O_2 during sampling. The liquor is diluted to prevent the precipitation of $CaSO_3 \cdot \frac{1}{2}H_2O$ and/or $CaSO_4 \cdot 2H_2O$ due to any supersaturation of these species. An aliquot of the oxidized diluted filtrate is passed through the hydrogen-form cation exchange column to convert all sulfates to sulfuric acid. The sample is then taken to dryness at 75°C to remove all volatile acids. An acid-base titration is then used to determine the concentration of sulfate. This concentration of sulfate represents the total sulfur species which include sulfate and sulfite.

All acids not volatile at 75°C interfere. In the equilibrium and kinetic studies, the only acids present in the sample after passage through the ion exchange column will be HCl and H_2SO_4. HCl is volatile at 75°C and should not interfere. The only other interference in the procedure would be any free ammonia present in the laboratory.

Laboratory Equipment

(1) Ion-exchange columns with internal diameter of 1.2 cm and 20 cm high are used. These should be equipped with sintered glass filter and stopcock control. A 25 ml reservoir bulb at the top of column is convenient.

(2) Microburet, 10 ml with 0.02 ml graduations.

(3) pH meter

(4) Graduated 100 ml beakers

(5) Hot plate and steam bath (75°C); surface thermometer (0-110°C)

(6) Pipets

Reagents

(1) Strong acid resin, 100-200 mesh size, hydrogen form (Styrene-divinylbenzene copolymer, 8% crosslinkage, with sulfonic functional group). Possible choices are Dowex 50W, Amberlite CG-120, or Rexyn 101 (Fisher brand).

(2) 5 M hydrochloric acid for regenerating the resin

(3) Hydrogen peroxide (30%)

(4) Standard sodium hydroxide (0.05-0.1 N). Commercially available standard solution concentrate may be used.

(5) pH 4 Buffer to standardize pH meter

Preparation of Ion Exchange Column

Place a strong acid-type resin, 100-200 mesh size, into a beaker and mix with water. If a cloudy suspension occurs, decant the liquid several times to remove fine resin particles which may otherwise pass through the columns during the sulfate determinations.

Transfer 20-25 ml of resin as a slurry through a funnel into the column, and drain sufficient water to settle the resin bed. The resin bed should be at least 17 cm high. Add more resin as required. Stopper the top of the column and shake it horizontally with 10 ml of water. This step releases the air bubbles and renders the resin bed homogeneous. For optimum packing, allow the resin to settle for at least 5 minutes before draining. Air voids below the sintered disk may be eliminated by backwashing the column (with or without resin). If the resin needs to be regenerated, pass 50 ml of 5 M hydrochloric acid through the column and rinse with 50 ml of water.

The ion exchange column is ready to process at least seven 10 ml samples of a cation concentration normally encountered in limestone based SO_2 scrubbers. However, if the resin is mixed after a sample has been processed, it is necessary to regenerate the resin. The bottom 6 cm height of the resin column must be completely in the hydrogen form. Any other cations present on the resin within this region would be eluted during the processing of samples, resulting in low sulfur values.

If a large number of columns are to be used, it is recommended that the resin be regenerated in one batch using a larger column. Less time and hydrochloric acid would be required. The regenerated resin may be stored as a slurry in bottles and be transferred, when needed, to smaller columns. Spent resin can be stored similarly until a sufficient amount is accumulated to make its regeneration in a big column worthwhile.

After the resin is stored for several days, the supernatant liquid may acquire a yellow tinge. This "color throw" from the resin is easily removed by rinsing in a column. When eluting with 5 M hydrochloric acid, the extent of regeneration may be verified by evaporating about 5 ml of effluent in a beaker on a hot plate. If no residue is obtained, the resin is completely regenerated.

Procedure for the Determination of Sulfate

(1) Allow the liquid in the column to drain to the top of the resin bed. Introduce a sample aliquot containing 0.02-0.25 mmole total sulfur to the column. A 10 ml aliquot is preferable. The total cation concentration (including H^+) should be less than 0.7 equiv./liter.

(2) Collect the effluent in a graduated 100 ml beaker. Allow the column to drain on top of resin bed. When 100-200 mesh resin is used surface tension is sufficient to keep liquid on resin and thus prevent the formation of air pockets in column. Rinse the

column reservoir with 5-10 ml of water, using a wash bottle, and drain again. Rinse the resin column with an additional 40 ml of water. If a 10-ml aliquot was used in step (a), collect a total of 60 ml of effluent in the beaker. The column is ready for another sample.

(3) Place the beaker on a hot plate and evaporate the solution down to 5 ml. Do not boil or allow the sample to go dry on the hot plate. If the effluent contains a noticeable amount of resin, it should be filtered prior to the evaporation step. A suction funnel may be used.

(4) Place the sample in a water bath at 75°C for 2 hours, or until all the volatile acids have evaporated (odor test). The residue should appear oily with no trace of solids. Evaporation should be made in an area free from ammonia and other vapors that may react with the acid mixture. It is acceptable to leave samples overnight in the water bath at 75°C.

(5) Dissolve the residue with a few ml of water, and titrate with 0.0500 N sodium hydroxide until the pH is 4.6. Both hydrogens in sulfuric acid are titrated at this pH. The effect of a small amount of carbonate in the standard base and also that of atmospheric

carbon dioxide is minimized by stopping the titration at pH = 4.6.

Calculation for Total Sulfur for Liquid-Phase Samples Analyzed by Ion-Exchange Method

No significant amount of phosphate has been found in scrubbing liquors so the calculations outlined below assume that phosphate is absent.

$$C_s = \left(\frac{M_B V_B}{2V_s}\right) D_F$$

where,

C_s = concentration of total sulfur as sulfate (SO_3) in sample (moles/liter)

M_B = molarity of sodium hydroxide (moles/liter)

V_B = volume of sodium hydroxide required for titration (ml)

D_F = dilution factor (if any)

If the concentration of sulfate sulfur is desired then the values for sulfite (SO_2) must be known.

$$C_2 = C_3 - C_1$$

where,

C_2 = concentration of sulfate sulfur (moles SO_3/liter)

C_3 = concentration of total sulfur as sulfate, (SO_3) in sample (moles/liter)

C_1 = concentration sulfite sulfur (moles SO_2/liter)

Accuracy

The accuracy of the described method is within 1% for samples containing at least 0.1 mmole of sulfate. The presence of salt residues after the evaporation of samples usually results in low values for sulfate. When this occurs, it is suggested that the resin be regenerated or a larger column be used. High sulfate values are obtained if resin particles pass through the column into the effluent. However, the resin is easily recognized after evaporation, and the solution turns yellow when titrated with base.

For an independent quality control check, a sulfate standard (Na_2SO_4) or a reference solution containing a known concentration of $CaSO_4$ in the same range as the actual samples, should be passed through the ion-exchange column and titrated with the sodium hydroxide solution until the pH is 4.6.

2.4 Chloride

Chloride present in the liquid phase of the equilibrium and kinetics studies was determined by a manual potentiometric titration with a standard silver nitrate solution. The detection limit for the analysis is .02 mmoles/ℓ. The accuracy of the procedure at the 95% confidence level is ±2% over the range of 1-200 mmoles of chloride/ℓ.

Apparatus

Silver Electrode - a cup type, Fisher No. 13-639-122 is suitable - a solid silver cylinder may also be used.

Adaptor for Silver Electrode - designed to fit into pH meter connection designed for glass electrode and to accept pin from silver electrode.

Reference Electrode - a silver-silver chloride with a sodium sulfate bridge is recommended. Fisher No. 9-313-216 is an example which is commercially available.

pH Meter - any standard pH meter with a millivolt scale is suitable.

Microburet - 10 ml capacity

Magnetic Stirrer

Reagents

0.0200 M Silver Nitrate - Dilute 400 ml commercially prepared 0.1000 M silver nitrate standard solution to 2000 ml.

.1000 M Hydrochloric Acid - Prepare from standard solution concentrate or purchase this concentration of solution.

0.01 M Hydrochloric Acid - Dilute 100 ml 0.100 M hydrochloric acid to 1000 ml.

Acetate Buffer Solution (.4 M sodium acetate and 0.4 M acetic acid) - Dissolve 54.4 g $Na(C_2H_3O_2) \cdot 3\ H_2O$ in about 400 ml water. Add 24 ml glacial acetic acid and dilute to one liter.

Non-Ionic Detergent - Tergitol non-ionic NPX or equivalent

Concentrated Nitric Acid - Reagent grade

Sodium Nitrite - Reagent grade

Procedure for the Determination of Chloride

(1) Standardize pH meter to 0 millivolts while on standby and in the ± millivolts mode.

(2) Pipette a suitable aliquot (.01-.20 millimoles of chloride) into a 150 ml beaker containing a stirring bar.

(3) Dilute to approximately 50 ml with deionized water.

(4) Add approximately 50 ml of the acetate buffer solution.

(5) Add 3 drops of nonionic detergent.

(6) Stir and titrate with .0200 M silver nitrate to a potentiometric end-point of -260 millivolts.

Electrode Cleaning

Clean the metallic silver electrode before each series of titrations and after about 15 titrations if more are run at one time. Prepare the cleaning solution by adding 50 ml concentrated nitric acid, 50 ml water and 20 milligrams of sodium nitrate just before use. Dip the electrode in the cleaning solution for only a few seconds and wash thoroughly with D.I. water.

Calculations

Concentrations of chloride in solution can be calculated using the following formula.

$$C_a = \frac{(V_s - V_B)M}{V_A}$$

where,

C_a = concentration of chloride (moles/ℓ),

V_s = volume of silver nitrate for sample titration (ml),

V_B = volume of silver nitrate for blank titration (ml),

M = molarity of the silver nitrate solution, and

V_A = aliquot size of sample.

2.5 Aqueous CO_2

Carbonate in the liquid phase of the equilibrium and kinetic studies was determined by chemical analysis of the aqueous CO_2 sample utilizing a nondispersive infrared analyzer. The operational procedure of the instrument is described in detail in Radian Technical Note 200-403-50. The detection limit is .1 ppm CO_2 with the optimum range as 25-100 ppm CO_2 ± 3% accuracy.

In general, the aqueous CO_2 sample is injected with a microsyringe into an acid pool which liberates CO_2. The CO_2 liberated is then measured by the nondispersive infrared analyzer. The output of the analyzer is coupled with a recorder equipped with disc-chart integrator for determining the peak area (proportional to the amount of CO_2 injected). The peak area for the samples and standards along with calibration data is input into a linear least squares program. The program is used to determine the CO_2 concentrations of the injected samples in moles/liter.

Apparatus

(1) OIC total carbon system equipped with disc-chart integrator

(2) Hamilton injection syringe

(3) Injector ampules with seal and septum

(4) Glass drying tubes filled with fresh magnesium perchlorate

Reagents

(1) 10% KH_2PO_4 stock solution

(2) 6% H_3PO_4 stock solution

(3) Na_2CO_3 reagent grade

(4) Methyl red indicator

(5) Magnesium perchlorate, anhydrous flake

3.0 ANALYTICAL PROCEDURES FOR CHARACTERIZATION OF SOLIDS

Characterization of the precipitated solids was performed in three phases. The first phase consisted of chemical analysis to determine the chemical composition of the solids. The solids were then analyzed with X-ray diffraction techniques to identify any pure crystalline phases. Finally the solids were analyzed by infrared analysis to confirm X-ray analysis and to identify possible crystalline structures of coprecipitation product.

Chemical analyses of the solids consists of a solid sulfite analysis, specific sulfate analysis, solid carbonate analysis, and a solid dissolution from which calcium, magnesium, sodium and total sulfur were determined with the appropriate analytical procedures.

3.1 Solid Phase Sulfite

Solids obtained from the equilibrium and kinetic studies were analyzed for their sulfite concentration by an iodometric titration with sodium arsenite. The theory and sensitivity of the analysis is similar to the aqueous sulfur dioxide determination. However, the procedure has been modified to accommodate complete dissolution of sulfite without degradation of the iodine.

Procedure for Solid Sulfite Determination

(1) Weigh 0.06 g of solid sample to the nearest 0.1 mg.

(2) Pour 60 ml of pH 6 buffer solution into a 4 oz glass bottle with cap and add stirring bar.

(3) Pipet 10 ml of 0.1 N standard iodine solution into the bottle, cap and begin stirring.

(4) Add the weighed solid sample and recap.

(5) Stir for 30 minutes.

(6) Empty bottle quantitatively into a 150 ml beaker and titrate as described in the procedure for aqueous SO_2 (Section 2.2).

Calculations

The concentration (mmole/gram) of sulfite present in the solid sample can be determined by use of the following equation:

$$C = \frac{(B-S)M}{W}$$

where,

C = concentration of sulfite (in mmoles/g)

B = volume of arsenite used to titrate the blank in ml

S = volume of arsenite used to titrate the sample in ml

M = concentration of the sodium arsenite (moles/ℓ)

W = weight of sample used in grams

3.2 Specific Sulfate

This method allows a specific determination of the concentration of sulfate in the solids. This differs from techniques discussed earlier which determine sulfate by the difference between the total sulfur and the solid sulfite.

In the procedure, a representative sample of the solids is dissolved in 0.1 N HCl oxygen-free solution to quantitatively decompose the sulfite to SO_2 gas which is eluted by constant bubbling of CO_2 gas through the solution. When all SO_2 has been evolved, the acidic sulfate solution is quantitatively transferred to an ion-exchange column and the total sulfur procedure described in Section 2.3 is followed. The detection limit is 0.075 mmoles/g (0.01 mole fraction sulfate). The accuracy at any level is ±0.004 mmoles SO_4^{-2}(0.100 gram of solids).

/ Apparatus

(1) CO_2 tank - oxygen free

(2) CO_2 regulator

(3) gas manifold

(4) midget impingers

(5) hydrogen-form cation exchange columns

(6) hot plate

(7) 75°C water bath

(8) 100 ml beakers

(9) pH meter

(10) microburet

(11) magnetic stirrer and bar

(12) analytical balance

Reagents

(1) 0.1 N HCl

(2) 0.05 N NaOH (±0.0001 N)

Procedure

(1) Weigh 100 mg solid sample to the nearest 0.1 mg.

(2) Fill midget impinger with 20 ml of an acidic solution (0.1 N HCl) and purge with oxygen-free CO_2 gas for 10 minutes at a flow rate of 100 ml CO_2/min to remove dissolved oxygen from acidic solution.

(3) Quantitatively transfer 100 mg sample to midget impinger containing 20 ml of the oxygen-free 0.1 N HCl with a few ml (<5 ml) of oxygen-free DI H_2O.

(4) Purge with oxygen-free CO_2 for 30 minutes to strip the sulfur dioxide from the acidic solution.

(5) Quantitatively transfer acidic solution to hydrogen-form cation exchange columns and follow total sulfur procedure described in Section 2.3.

Calculations

The concentration of the solution (mmoles/g) may be calculated by use of the following formula.

$$C = \frac{N_B V_B}{2W}$$

where,

C = concentration of sulfate in the solids (mmole/g)

N_B = normality of the NaOH solution

V_B = volume of the NaOH solution used to titrate sample

W = weight of sample used

and 2 is the number of equivalents per mole (or meq/mmole) of the H_2SO_4 formed by the ion-exchange column.

3.3 Solid Carbonate

Carbonate present in the solid phase of the equilibrium and kinetic studies was determined by nondispersive infrared analysis. The apparatus, reagents and solution, preparation of standards, and calculations are described in Radian Technical Note 200-403-50. The following section will document the procedure used for the adaptation of the method for solid carbonate analysis.

Procedure

(1) Dry the filtered solids at least 48 hours at a maximum temperature of 60°C.

(2) Weigh out 200 mg (±0.01 mg) solids for analysis (30 mg $CaCO_3$ for standards) and transfer to 100 ml volumetric flask.

(3) Rinse neck of flask with CO_2 free DI H_2O (freshly boiled DI H_2O).

(4) Pipet 10 ml of freshly prepared CO_2 buffer into volumetric flask.

(5) Fill each volumetric flask to mark with CO_2 free DI H_2O.

(6) Add teflon magnetic stirring bar to each flask and stir for 30 minutes with flasks tightly stoppered.

(7) Remove stirring bar and rinse the clean 60 ml polypropylene bottle with small aliquot of sample.

(8) Fill sample bottles to neck, tighten cap and seal with tape until analysis.

(9) Run the samples and standards on the nondispersive infrared analyzer in the same method as employed in aqueous CO_2 determination with the exception of a modified acid pool (a mixture of 95 mls of 10% KH_2PO_4, 5 mls of 5% H_3PO_4, and 1 ml 30% H_2O_2).

Calculations

A computer program is utilized to calculate the concentration of carbonate in moles/liter of the solution injected into the analyzer. Utilization of the computer program is described in detail in Section 8 of Radian Technical Note 200-403-50. The following equation was used for calculation of the solid carbonate concentration in moles/gram.

$$C_1 = \frac{C_2 V}{W}$$

where,

C_1 = concentration of carbonate in solid sample (moles/gram)

C_2 = concentration (moles/liter) of carbonate of solution injected into analyzer (dissolution concentration)

V = volume of volumetric flask used in dissolution step (100 ml)

W = weight of solid sample dissolved in volumetric (∿200 mg)

3.4 Solid Dissolution

The following technique was used for dissolving solids recovered from the equilibrium and kinetic studies. It entails dissolving a known weight of dried solid in an acidic medium containing a sufficient amount of H_2O_2 to oxidize the sulfite to sulfate. Following filtration, the liquid may be analyzed for calcium, sodium, magnesium, and total sulfur according to technique described in Sections 2.1 and 2.3.

Apparatus

(1) 2 100 ml volumetric flasks

(2) 100 ml graduated cylinder

(3) 10 ml graduated cylinder

(4) 1 ml graduated pipet

(5) magnetic stirrer

Reagents

(1) HCl concentrated (12 Molar reagent grade)

(2) 1 M HCl (approximate) - 84 ml concentrated HCl diluted with D.I. H_2O to 1 liter

(3) hydrogen peroxide - 30%

Procedure

(1) Accurately weigh 0.200 g (±0.1 mg) of solids.

(2) Quantitatively transfer solids to a clean 100 ml volumetric flask.

(3) Add approximately 50 ml of DI water.

(4) Pipet 0.3 ml of 30% H_2O_2 into flask.

(5) Insert stirring bar and stir, tightly stoppered, for 10 minutes.

(6) Pipet 0.4 ml of 1 M HCl into the flask and stir for 30 minutes with stopper secure.

(7) Add by graduated cylinder an additional 5 ml of 1 M HCl and stir for an additional 30 minutes with stopper secure.

(8) Additional HCl may be added to the solution, remembering that the (H^+) adds to the total cation concentration.

(9) Remove the stirring bar and dilute to volume.

(10) Filter.

(11) Transfer to a clean 120 ml polypropylene bottle, cap and seal with tube until ready for use. All liquor analyses except for chloride may then be performed on the solid dissolution following procedures described in Section 2 of this report.

3.5 X-Ray Diffraction Analysis

Selected solids from the experimental runs were analyzed utilizing an automatic X-ray diffractometer to identify crystalline phases present in the precipitated solids with particular emphasis on the crystalline form of the solid phase sulfate. The intensity of the diffracted beam is recorded continuously on a strip chart and compared with published patterns and with reference standards prepared by Radian for identification.

Reference standards of calcium sulfite hemihydrate, calcium sulfate dihydrate and calcium sulfate hemihydrate were prepared under controlled laboratory conditions and analyzed chemically for purity. Reference standards and solid samples were ground with mortar and pestle, and classified. Solids smaller than 44 micrometers were stored in vials in an inert atmosphere until analysis. X-ray diffraction patterns of the samples were compared to the standards for identification.

3.6 Infrared Analysis of the Solid Phase

Infrared analyses were performed on all experimental solids to distinguish between pure sulfate compounds and sulfate contained within the sulfite crystalline lattice. Spectra of standards prepared in the laboratory and published spectra were used for reference in interpretation of the spectra of experimental solids.

APPENDIX E

ANALYTICAL RESULTS; REACTOR MATERIAL BALANCES, SOLID MATERIAL BALANCES, AND COMPUTER EQUILIBRIUM DATA OF LABORATORY EXPERIMENTAL RUNS

Prepared by:
Benjamin F. Jones
Larry A. Rohlack

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1.0 INTRODUCTION

This appendix presents the experimental data, calculations, and material balances for experimental kinetic runs 44-71, and equilibrium extraction runs 1-12. Extensive analysis of experimental data has been performed on each of these experimental runs. Four data sheets have been required to fully characterize each run. The first sheet contains a summary of analytical results, operating conditions and computer results. The second sheet presents the material balance calculations around the reactor. The third sheet presents the material balances for the solids only. The results of computations by Radian's ionic equilibrium program are printed and presented as the fourth data sheet.

The following four sections are provided as explanations for the content of each of the four data sheets. Equations are provided as needed for the calculations presented in the data sheets. The precipitation apparatus utilized in the kinetic studies is depicted in Figure 1. This diagram will facilitate the understanding of the experimental data and of the mass balances which follow.

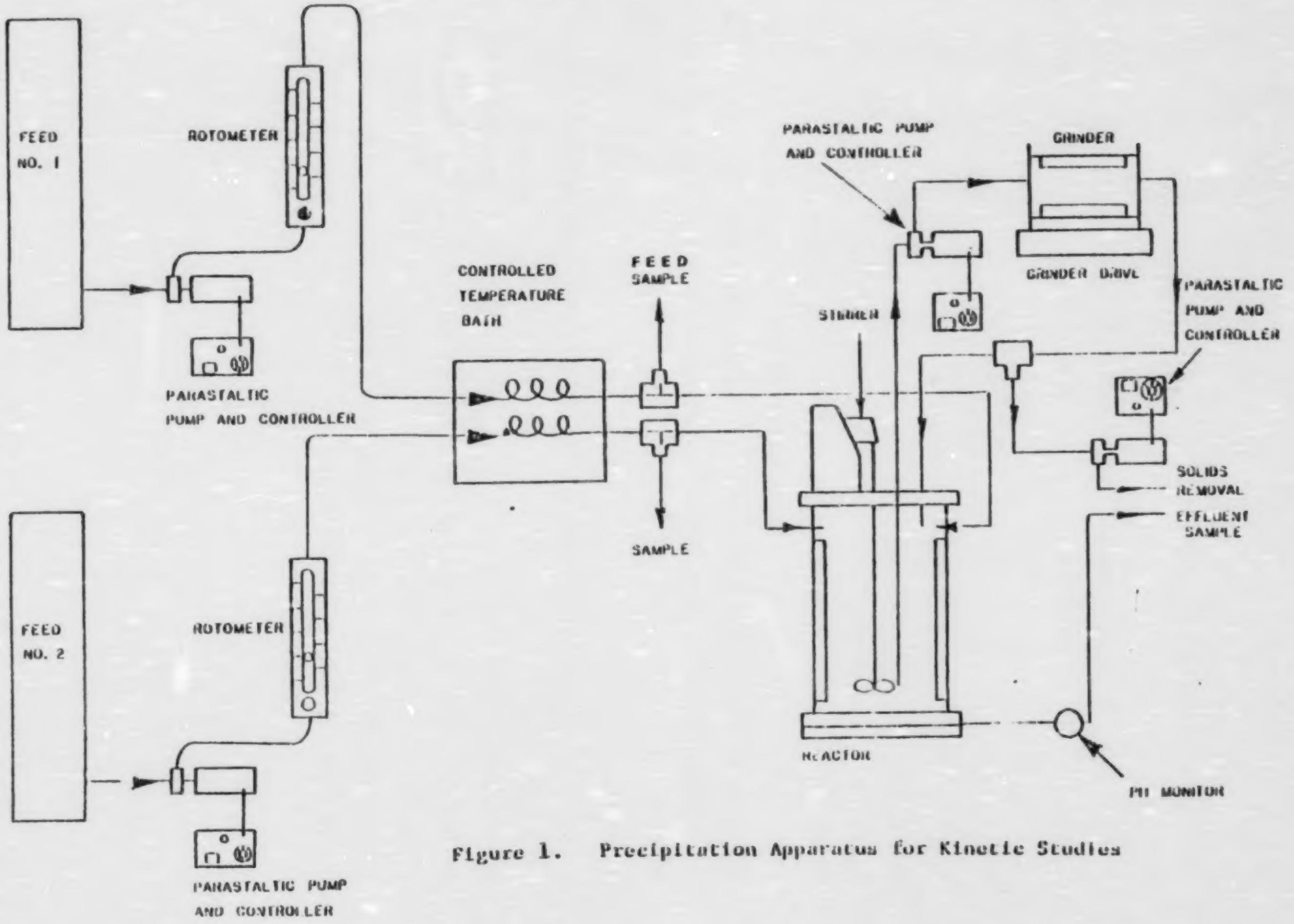
FEED
NO. 1
ROTOMETER
PARASTALTIC
PUMP AND CONTROLLER
FEED
NO. 2
ROTOMETER
PARASTALTIC PUMP
AND CONTROLLER
CONTROLLED
TEMPERATURE
BATH
FEED
SAMPLE
SAMPLE
PARASTALTIC PUMP
AND CONTROLLER
GRINDER
GRINDER DRIVE
STIRRER
PARASTALTIC
PUMP AND
CONTROLLER
SOLIDS
REMOVAL
EFFLUENT
SAMPLE
REACTOR
PH MONITOR

Figure 1. Precipitation Apparatus for Kinetic Studies

2.0 ANALYTICAL RESULTS, OPERATING DATA, AND COMPUTER SUMMARY

An example of the first data sheet for each set is shown on the following page.

2.1 Analytical Results

Analytical concentrations are presented for the two feed streams into the reactor and the effluent and solids leaving the reactor. These concentrations in millimole per liter represent the average values of duplicate or triplicate determinations. Major ions, including calcium, magnesium, sodium, chloride, carbonate, total sulfur, sulfite, and sulfate, have been determined by the analytical techniques documented in Appendix C.

A set of quality control analytical standards were prepared. These standards were analyzed each time a set of experimental samples was characterized. The concentration of the ions in the standards were as follows:

Calcium - 50 mmole/liter
Magnesium - 8 mmole/liter
Sodium - 10.6 mmole/liter
Chloride - 99.5 mmole/liter
Total sulfur and sulfate - 18.8 mmole/liter

The concentration of the standard as measured with each set of experimental samples is then compared to the actual concentration as presented above. The resulting standard deviation is calculated. This standard deviation in % is then presented in the column labeled "Standards" under the analytical results section of the first data sheet.

RUN NO. 44

DATE 1/27/76

$e^{-T/\tau}$ .15

ANALYTICAL RESULTS

Species	Standards (% Deviation)	Ca^{+} Feed (mmole/l)	SO$_3^{-2}$ Feed (mmole/l)	Effluent (mmole/l)	Solids (mmole/g)
Ca^{+2}	-.1	64.3	--	25.7	7.24
Mg^{+2}	0	--	1190.	560	.035
Na^{+1}		6.89	60.6	30.4	.02
Cl^{-1}	.3	131.	1380.	766	--
CO$_3^{-2}$	--	--	--	--	--
Ts^{-2}	1.0	--	436.	217.	2.02
SO$_3^{-2}$	--	--	45.6	17.1	5.43
SO$_4^{-2}$	1.0	--	390.	200.	1.07

OPERATING DATA

Time (min)	pH	Temp. (^{o}C)	SO$_3^{-2}$ (mmole/l)	Solids Removal (ml/min)	Solids (wt%)	Solids (g)
30	6.43	47.3	17.3	32	.25	8.2
60	6.31	48.0	17.7	33.	.26	8.6
90	6.29	48.6	17.6	29.	.29	9.3
150	6.25	50	17.3	31.	.32	10.4
180	6.22	50	17.10	30.	.29	9.31

COMPUTER RESULTS

Ionic Strength	Residual Electroneutrality	Relative Saturation			Mole Fraction	
		CaSO$_3\cdot\frac{1}{2}$H$_2$O	CaSO$_4\cdot$2H$_2$O	CaSO$_4\cdot\frac{1}{2}$H$_2$O	SO$_3^{-2}$	SO$_4^{-2}$
1.35	-.063	7.4	1.01	0.46	.33	.17

2.2 Operating Data

Operating conditions are monitored throughout each experimental run to determine approach to steady state and to determine how close the actual operating conditions are to the design of the experiment. Key parameters which are monitored are pH, temperature, sulfite concentration, solids removal rate, and concentration of solids in the reactor. The concentration of the solids is presented as the total mass of seed crystals and as a % of the total weight of the slurry.

2.3 Computer Summary

Key computations of the Radian aqueous ionic equilibrium program are summarized in this section of data sheet #1. The ionic strength, residual electroneutrality, relative saturation of calcium sulfite hemihydrate, calcium sulfate dihydrate, and calcium sulfate hemihydrate are presented. The residual electroneutrality is a rough indication of the accuracy of the input concentrations of the major species. The % error is obtained by dividing the residual electroneutrality by the ionic strength and multiplying the quotient by one hundred.

2.4 Mole Fraction of Sulfite and Sulfate in the Precipitated Solids

The mole fractions of the precipitated sulfite and sulfate were calculated by the following equations:

$$X_{SO_3^{-2}} = \frac{Cp(SO_3^{-2})}{Cp(SO_4^{-2}) + Cp(SO_3^{-2})}$$ and

$$X_{SO_4^{-2}} = \frac{Cp(SO_4^{-2})}{Cp(SO_4^{-2}) + Cp(SO_3^{-2})}$$ where

$X_{SO_3^{-2}}$ = sulfite mole fraction; i.e., the ratio of sulfite in the precipitated solids to that of the total sulfur in the precipitated solids.

$Cp(SO_3^{-2})$ = concentration of precipitated sulfite in millimoles of sulfite per gram of precipitated solid.

$Cp(SO_4^{-2})$ = concentration of precipitated sulfate in millimoles of sulfate per gram of precipitated solid.

$X_{SO_4^{-2}}$ = sulfate mole fraction or the ratio of precipitated sulfate to that of the total sulfur precipitated.

The concentration (Cp) of the solid ion of interest, either calcium, sulfite or sulfate, is calculated using the following equation.

$$Cp = \frac{CeMe - CsMs}{Me - Ms}$$ where

Ce = concentration (mmole/gram) of species (calcium, sulfite, or sulfate) present in the solids at the end of the experimental run.

Me = total mass (grams) of solids present in the reactor at the end of the run

$Me = We \times Vr$ where

We = concentration of solids (g/ℓ) at end of run
Vr = volume of reactor in liters = 3.25 liters

Cs = concentration (mmole/gram) of species present in the seed charge at the beginning of the run

Ms = mass of initial seed charge present in the reactor at the end of the run.

The mass of the initial seed charge present in the reactor at the end of the run can be calculated by the following equations:

$Ms = Mi \times e^{-T/\tau}$ where

Ms = mass of initial seed charge present at end of run

Mi = mass of initial seed charge in reactor at the beginning of run

$e^{-T/\tau}$ = fraction of initial seed charge remaining in reactor at end of run

T = elapsed time of run (minutes)

$\tau = \frac{Vr}{Fs}$ = residence time of solids in reactor where

Vr = reactor volume = 3.25 liters
Fs = solids removal rate (liters/min)

3.0 REACTOR MATERIAL BALANCES

Material balances for the reactor are presented on the second data sheet for each run. An example of the sheet is shown on the following page. In addition, precipitation rate for each species calcium, sulfite, and sulfate have been normalized to the precipitation rate of the total solids.

Material balances have been calculated for each of the major ions of interest and include calcium, sodium, magnesium chloride, sulfite, sulfate, and carbonate. This is accomplished by calculating the millimolar flow rate of each species into the reactor and comparing it to the corresponding rate leaving the reactor.

For the inlet, these rates are calculated for each feed stream by multiplying the volume flow rate (ml/min) by the concentration of species (mmole/ml). The resulting millimolar rates of each ion for two feed streams are then summed.

For the outlet, similar calculations are made for the millimolar rate in the liquid phase. These effluent liquid phase millimolar rates are then added to the corresponding effluent solid phase millimolar flow rate. Solid phase millimolar flow rate is determined by multiplying the solid phase concentration (millimoles/gram) by the product of the slurry, removal rate (liters/minutes), and the solids concentration (grams/liter).

After calculating the precipitation rate (mmole/min) of each ion of interest (calcium, sulfite and sulfate) the rate is normalized to the total solids precipitation rate (grams/minute). This is accomplished by dividing the individual rate (mmole/min)

REACTOR MATERIAL BALANCE CALCULATIONS

Run # 44 Date 1/27/76

INLET	A	B	Σ
Flow Rate (ml/min)	50	50	100
Ca^{+2} (mmole/min)	3.22	----	3.22
Mg^{+2} (mmole/min)	----	39.6	39.6
Na_2^{+2} (mmole/min)	.35	3.03	3.38
Cl^{-1} (mmole/min)	6.54	69.1	75.6
CO_3^{-2} (mmole/min)	----	----	----
SO_3^{-2} (mmole/min)	----	2.28	2.28
SO_4^{-2} (mmole/min)	----	19.5	19.5

OUTLET	Liquid	Solid	Σ
Flow Rate (ml/min)	100	0.098 (g/min)	
Ca^{+2} (mmole/min)	2.57	0.71	3.28
Mg^{+2} (mmole/min)	36.	.003	36.
Na_2^{+2} (mmole/min)	3.04	.002	3.04
Cl^{-1} (mmole/min)	76.6	----	76.6
CO_3^{-2} (mmole/min)	----	----	----
SO_3^{-2} (mmole/min)	1.71	.63	2.34
SO_4^{-2} (mmole/min)	20.0	.105	20.1

PREC. RATE	mmole/min	mmole/g	grams/min
Solid			0.098
Ca^{+2}	0.63	7.24	.090
SO_3^{-2}	.57	6.43	.089
SO_4^{-2}	-0.48	1.07	-0.449

by its concentration in the solid (mmole/gram). This normalizes each of the rates and allows another independent check of the accuracy of the analytical measurements and flow rate measurements.

4.0 SOLID MATERIAL BALANCES

Material balances were also calculated for the solid phase alone. An example data sheet is presented on the following page. Balances were calculated by multiplying the solid concentration of each ion (mmole/gram) by its molecular weight (g/mmole) to obtain its fractional equivalent of the total solid. The water content of the solids was determined by assuming ½ mole of water for each mole of sulfite and ½ mole of water for each mole of sulfate present. These fractions were then summed and compared to an optimum balance of one gram.

SOLIDS MATERIAL BALANCE

Run # 44 Date 1/27/76

	g/mmole	mmole/gram	g/gram
Ca^{+2}	.040	7.24	0.290
Mg^{+2}	.024	.035	.001
Na_2^{+2}	.046	.02	.001
Cl^{-1}	.035	----	----
CO_3^{-2}	.060	----	----
SO_3^{-2}	.080	6.43	.514
SO_4^{-2}	.096	1.07	.103
$\frac{1}{2}H_2O$	.009	7.50	.068
			Σ 0.977

5.0 COMPUTER RESULTS

As stated earlier, the pH, temperature, and molar concentrations of the major cations and anions are input into Radian's aqueous ionic equilibrium program. This program takes the inputs for each case, together with the relevant dissociation and solubility product constants, and calculates pertinent equilibrium data. Activities of the major ions and ion pairs and the relative saturation of relevant solid species are calculated. In addition, the ionic strength and residual electroneutrality are calculated and printed.

EXPERIMENTAL DATA

RUN NO. 44

DATE 1/27/76

$e^{-T/\tau}$ .15

ANALYTICAL RESULTS

Species	Standards (% Deviation)	Ca^{+} Feed (mmole/l)	SO_3^{-2} Feed (mmole/l)	Effluent (mmole/l)	Solids (mmole/g)
Ca^{+2}	-.1	64.3	--	25.7	7.24
Mg^{+2}	0	--	1190.	560	.035
Na_2^{+1}		6.89	60.6	30.4	.02
Cl^{-1}	.3	131.	1380.	766	--
CO_3^{-2}	--	--	--	--	--
Ts^{-2}	1.0	--	436.	217.	7.02
SO_3^{-2}	--	--	45.6	17.1	6.43
SO_4^{-2}	1.0	--	390.	200.	1.07

OPERATING DATA

Time (min)	pH	Temp. (°C)	SO_3^{-2} (mmole/l)	Solids Removal (ml/min)	Solids (wt%)	Solids (g)
30	6.43	47.3	17.5	32	.25	8.2
60	6.31	48.0	17.7	33.	.26	8.6
90	6.29	48.6	17.6	29.	.29	9.3
150	6.25	50	17.3	31.	.32	10.4
180	6.22	50	17.10	50.	.29	9.31

COMPUTER RESULTS

Ionic Strength	Residual Electroneutrality	Relative Saturation			Mole Fraction	
		$CaSO_3 \cdot \frac{1}{2}H_2O$	$CaSO_4 \cdot 2H_2O$	$CaSO_4 \cdot \frac{1}{2}H_2O$	SO_3^{-2}	SO_4^{-2}
1.35	-.063	7.4	1.01	0.46	.33	.17

REACTOR MATERIAL BALANCE CALCULATIONS

Run # 44   Date 1/27/76

INLET		A	B	Σ
Flow Rate (ml/min)		50	50	100
Ca^{+2}	(mmole/min)	3.22	----	3.22
Mg^{+2}	(mmole/min)	----	59.6	59.6
Na_2^{+2}	(mmole/min)	.35	3.03	3.38
Cl^{-1}	(mmole/min)	6.54	69.1	75.6
CO_3^{-2}	(mmole/min)	----	----	----
SO_3^{-2}	(mmole/min)	----	2.28	2.28
SO_4^{-2}	(mmole/min)	----	19.5	19.5

OUTLET		Liquid	Solid	Σ
Flow Rate (ml/min)		100	0.098 (g/min)	
Ca^{+2}	(mmole/min)	2.57	0.71	3.28
Mg^{+2}	(mmole/min)	56.	.003	56.
Na_2^{+2}	(mmole/min)	3.04	.002	3.04
Cl^{-1}	(mmole/min)	76.6	----	76.6
CO_3^{-2}	(mmole/min)	----	----	----
SO_3^{-2}	(mmole/min)	1.71	.63	2.34
SO_4^{-2}	(mmole/min)	20.0	.105	20.1

PREC. RATE	mmole/min	mmole/g	grams/min
Solid			0.098
Ca^{+2}	0.65	7.24	.090
SO_3^{-2}	.57	6.43	.089
SO_4^{-2}	-0.48	1.07	-0.449

SOLIDS MATERIAL BALANCE

Run # 44 Date 1/27/76

	g/mmole	mmole/gram	g/gram
Ca^{+2}	.040	7.24	0.290
Mg^{+2}	.024	.035	.001
Na_2^{+2}	.046	.02	.001
Cl^{-1}	.035	----	----
CO_3^{-2}	.060	----	----
SO_3^{-2}	.080	6.43	.514
SO_4^{-2}	.096	1.07	.103
$\frac{1}{2}H_2O$	.009	7.50	.068
			Σ 0.977

KINETIC RUN 44

```
03 MAR 76    14:15:37.278

                         INPUT SPECIES (MOLES)          TEMPERATURE    50.000 DEG. C.
              H2O  = 5.55082+01
              CAO  = 2.57000-02                 HCL  = 7.68300-01
              MGO  = 5.11000-01                 CO2  = 0.00000
              NA2O = 3.04000-02                 N2O3 = 0.00000
                                                N2O5 = 0.00000
                                                SO2  = 1.71000-02
      PH =  6.230                               SO3  = 2.29000-01

      SUPERSATURATION ALLOWED

                      AQUEOUS SOLUTION EQUILIBRIA
  COMPONENT           MOLALITY           ACTIVITY         ACTIVITY COEFFICIENT

   H+                 4.645-07           5.887-07             1.267+00
   H2O                                                        9.764-01
   H2SO3              8.949-08           1.130-07             1.267+00
   HSO3-              2.553-03           1.514-03             5.928-01
   HSO4-              7.361-07           6.240-07             8.501-01

   CA++               1.805-02           4.566-03             2.430-01
   CAOH+              1.342-08           1.154-08             8.501-01
   CASO3              1.339-03           1.692-03             1.267+00
   CASO4              5.230-03           6.632-03             1.267+00

   MG++               3.745-01           1.170-01             3.122-01
   MGOH+              6.497-08           5.523-08             8.501-01
   MGSO3              1.210-02           1.532-02             1.267+00
   MGSO4              1.189-01           1.506-01             1.267+00

   NA+                5.871-02           4.258-02             7.252-01
   NAOH               8.236-11           1.042-10             1.267+00
   NASO3-             1.097-04           9.327-05             8.501-01
   NASO4-             1.559-03           1.325-03             8.501-01

   OH-                1.176-07           9.996-08             8.501-01
   CL-                7.608-01           4.334-01             5.697-01




   SO3--              8.858-04           1.095-04             1.235-01
   SO4--              7.290-02           5.127-03             7.033-02
  COMPONENT           MOLALITY        ACTIVITY PRODUCT  RELATIVE SATURATION

   CA(OH)2(S)         0.000              3.779-17             1.138-11
   CASO3(S)           0.000              4.942-07             7.306+00
   CASO4(S)           0.000              2.232-05             1.013+00
   MG(OH)2(S)         0.000              9.724-16             1.032-04
   MGSO3(S)           0.000              1.198-05             2.978-01
  PSO2 = 2.17441-07  ATM.

              MOLECULAR WATER = 1.00000+00 KGS.

            IONIC STRENGTH = 1.35928+00       RES. E.N. =  -6.309-02
```

RUN NO. 45
DATE 2/2/76

$e^{-T/\tau}$ .06

ANALYTICAL RESULTS

Species	Standards (% Deviation)	Ca^{+} Feed (mmole/l)	SO_3^{-2} Feed (mmole/l)	Effluent (mmole/l)	Solids (mmole/g)
Ca^{+2}	-.1	61.9		27.7	5.58
Mg^{+2}	0	--	1030.	529.	.18
Na^{+1}	-.8	6.70	40.7	23.6	.01
Cl^{-1}	.3	125.	1400.	819.	--
CO_3^{-2}	--	--	--	--	--
Ts^{-2}	1.0	--	418.	222.	5.6
SO_3^{-2}	--	--	33.3	14.9	1.52
SO_4^{-2}	1.0	--	385.	207.	4.40

OPERATING DATA

Time (min)	pH	Temp. (°C)	SO_3^{-2} (mmole/l)	Solids Removal (ml/min)	Solids (wt%)	Solids (g)
30	6.30	47.3	16.3			
120	6.19	48.8	16.2	18.5	.14	4.5
180	6.19	51.0	15.8	16.9	.16	5.1
360	6.18	49.9	15.9	21.4	.19	6.0
420	6.18	50.0	15.5	--	.20	6.4

COMPUTER RESULTS

Ionic Strength	Residual Electroneutrality	Relative Saturation			Mole Fraction	
		$CaSO_3 \cdot \frac{1}{2}H_2O$	$CaSO_4 \cdot 2H_2O$	$CaSO_4 \cdot \frac{1}{2}H_2O$	SO_3^{-2}	SO_4^{-2}
1.40	.115	6.7	1.15	0.52	0.20	0.80

REACTOR MATERIAL BALANCE CALCULATIONS

Run # 45 Date 2/02/76

INLET		A	B	Σ
Flow Rate (ml/min)		50	50	100
Ca^{+2}	(mmole/min)	3.10	----	3.10
Mg^{+2}	(mmole/min)	----	51.5	51.5
Na_2^{+2}	(mmole/min)	.34	2.04	2.38
Cl^{-1}	(mmole/min)	6.26	70.3	76.6
Ts	(mmole/min)	----	20.9	20.9
SO_3^{-2}	(mmole/min)	----	1.67	1.67
SO_4^{-2}	(mmole/min)	----	19.2	19.2

OUTLET		Liquid	Solid	Σ
Flow Rate (ml/min)		100	0.042 (g/min)	
Ca^{+2}	(mmole/min)	2.77	0.235	3.01
Mg^{+2}	(mmole/min)	52.9	.008	52.9
Na_2^{+2}	(mmole/min)	2.36	.0004	2.36
Cl^{-1}	(mmole/min)	81.9	----	81.9
Ts	(mmole/min)	22.2	0.25	22.5
SO_3^{-2}	(mmole/min)	1.49	.064	1.55
SO_4^{-2}	(mmole/min)	20.7	.188	20.9

PREC. RATE	mmole/min	mmole/g	grams/min
Solid			0.042
Ca^{+2}	0.33	5.58	.059
SO_3^{-2}	.18	1.52	.118
SO_4^{-2}	-2.3	4.40	- .523

SOLIDS MATERIAL BALANCE

Run # 45 Date 2/2/76

	g/mmole	mmole/gram	g/gram
Ca^{+2}	.040	5.58	0.223
Mg^{+2}	.024	.18	.004
Na_2^{+2}	.046	.01	.001
Cl^{-1}	.035	----	----
CO_3^{-2}	.060	----	----
SO_3^{-2}	.080	1.52	.122
SO_4^{-2}	.096	4.40	.423
$\frac{1}{2}H_2O$	.009	5.92	.053
$1\frac{1}{2}H_2O$	.027	4.40	.119
		Σ	.945

KINETIC RUN 45

```
03 MAR 79    14:15:35,200                                   TEMPERATURE    50,000 DEG. C.
                                   INPUT SPECIES (MOLES)

                 H2O  = 5,55082+01                    HCL  = 8,19000-01
                 CAO  = 2,77207-02                    CO2  = 0,00000
                 MGO  = 5,20200-01                    N2O3 = 0,00000
                 NA2O = 2,38000-02                    N2O5 = 0,00000
                                                      SO2  = 1,40000-02
                                                      SO3  = 2,15000-01

        PH =  6,1820

        SUPERSATURATION ALLOWED

                           AQUEOUS SOLUTION EQUILIBRIA

       COMPONENT          MOLALITY           ACTIVITY     ACTIVITY COEFFICIENT

        H+                5,204-07           6,607-07           1,297+00
        H2O                                                     9,753-01
        H2SO3             9,324-08           1,192-07           1,278+00
        HSO3-             2,391-03           1,412-03           5,907-01
        HSO4-             9,494-07           7,314-07           8,618-01

        CA++              2,247-02           4,979-03           2,437-01
        CAOH+             1,302-09           1,122-09           8,618-01
        CASO3             1,197-03           1,530-03           1,278+00
        CASO4             5,903-03           7,544-03           1,278+00

        MG++              3,854-01           1,224-01           3,108-01
        MGOH+             5,929-06           5,109-06           8,618-01
        MGSO3             1,038-02           1,327-02           1,278+00
        MGSO4             1,283-01           1,640-01           1,278+00

        NA+               4,553-02           3,313-02           7,278-01
        NAOH              5,646-17           7,219-17           1,278+00
        NASO3-            7,294-05           6,034-05           8,618-01
        NASO4-            1,251-03           1,078-03           8,618-01

        OH-               9,397-08           8,098-08           8,618-01
        CL-               4,132-01           4,013-01           9,873-01




        SO3--             7,480-04           9,127-05           1,217-01
        SO4--             7,796-02           5,358-03           6,873-02

       COMPONENT          MOLALITY       ACTIVITY PRODUCT  RELATIVE SATURATION

        CA(OH)2(S)        0,000              3,258-17           9,818-12
        CASO3(S)          0,000              4,470-07           8,863+00
        CASO4(S)          0,000              2,533-05           1,150+00
        MG(OH)2(S)        0,000              9,925-16           8,528-05
        MGSO3(S)          0,000              1,034-05           1,794-01

        PSO2 = 2,27900-07  ATM.

                          MOLECULAR WATER = 1,02730+00 KGS.

                     IONIC STRENGTH = 1,40221+00        RES. E.N. =  -1,150-01
```

RUN NO. 46

DATE 2/3/76

$e^{-T/\tau}$ .012

ANALYTICAL RESULTS

Species	Standards (% Deviation)	Ca^{+} Feed (mmole/l)	SO_3^{-2} Feed (mmole/l)	Effluent (mmole/l)	Solids (mmole/g)
Ca^{+2}	-.1	61.9		24.6	7.12
Mg^{+2}	0	--	506.	248	.015
Na^{+1}	-.8	6.7	36.4	19.9	.01
Cl^{-1}	.3	126.	647.	384	--
CO_3^{-2}	--	--	--	--	--
Ts^{-2}	1.0	--	273.	128.	6.70
SO_3^{-2}	--	--	34.5	10.3	6.22
SO_4^{-2}	1.0	--	240.	118.	1.08

OPERATING DATA

Time (min)	pH	Temp. (°C)	SO_3^{-2} (mmole/l)	Solids Removal (ml/min)	Solids (wt%)	Solids (g)
30	6.4	48	12.7	75.5		
60	6.3	48.5	11.9	75.5	.22	7.1
110	6.28	49.1	11.7	75.5		
190	--	--	10.3	--	.12	4.0

COMPUTER RESULTS

		Relative Saturation			Mole Fraction	
Ionic Strength	Residual Electroneutrality	$CaSO_3 \cdot \frac{1}{2}H_2O$	$CaSO_4 \cdot 2H_2O$	$CaSO_4 \cdot \frac{1}{2}H_2O$	SO_3^{-2}	SO_4^{-2}
0.715	-.053	6.7	0.95	0.42	.85	.15

REACTOR MATERIAL BALANCE CALCULATIONS

Run # 46 Date 2/03/76

INLET		A	B	Σ
Flow Rate (ml/min)		50	50	100
Ca^{+2}	(mmole/min)	3.10	----	3.10
Mg^{+2}	(mmole/min)	---	25.3	25.3
Na_2^{+2}	(mmole/min)	.34	1.82	2.16
Cl^{-1}	(mmole/min)	6.32	32.4	38.7
Ts	(mmole/min)	----	----	13.7
SO_3^{-2}	(mmole/min)	----	1.73	1.73
SO_4^{-2}	(mmole/min)	----	11.9	11.9

OUTLET		Liquid	Solid	Σ
Flow Rate (ml/min)		100	0.093 (g/min)	
Ca^{+2}	(mmole/min)	2.46	0.664	3.12
Mg^{+2}	(mmole/min)	24.8	.0014	24.8
Na_2^{+2}	(mmole/min)	1.99	.0009	1.99
Cl^{-1}	(mmole/min)	38.4	----	38.4
Ts	(mmole/min)	12.8	----	--
SO_3^{-2}	(mmole/min)	1.03	.580	1.61
SO_4^{-2}	(mmole/min)	11.8	.10	11.9

PREC. RATE	mmole/min	mmole/g	grams/min
Solid			0.093
Ca^{+2}	0.64	7.12	.090
SO_3^{-2}	.70	6.22	.113
SO_4^{-2}	.16	.70	.229

SOLIDS MATERIAL BALANCE

Run # 46 Date 2/03/76

	g/mmole	mmole/gram	g/gram
Ca^{+2}	.040	7.12	0.285
Mg^{+2}	.024	.015	.001
Na_2^{+2}	.046	.01	.001
Cl^{-1}	.035	----	----
CO_3^{-2}	.060	----	----
SO_3^{-2}	.080	6.22	.498
SO_4^{-2}	.096	1.08	.104
$\frac{1}{2}H_2O$	.009	6.92	.062
			Σ .951

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KINETIC RUN 46

```
03 MAR 76     14:15:39.980                                  TEMPERATURE    49.100 DEG. C.
                                  INPUT SPECIES (MOLES)

                H2O  = 5.55062+01                  HCL  = 3.84000-01
                CAO  = 2.40000-02                  CO2  = 0.00000
                MGO  = 2.40000-01                  N2O3 = 0.00000
                NA2O = 1.99000-02                  N2O5 = 0.00000
                                                   SO2  = 1.03000-02
                                                   SO3  = 1.18000-01

     PH =  6.2800


     SUPERSATURATION ALLOWED

                    AQUEOUS SOLUTION EQUILIBRIA

     COMPONENT          MOLALITY             ACTIVITY      ACTIVITY COEFFICIENT

      H+                5.425-07             5.247-07             9.668-01
      H2O                                                         9.863-01
      H2SO3             7.970-08             9.031-08             1.133+00
      HSO3-             2.169-03             1.372-03             6.318-01
      HSO4-             7.637-07             5.657-07             7.408-01

      CA++              1.783-02             4.039-03             2.265-01
      CAOH+             1.480-08             1.096-08             7.408-01
      CASO3             1.343-03             1.522-03             1.133+00
      CASO4             5.344-03             6.056-03             1.133+00

      MG++              1.015-01             5.640-02             2.778-01
      MGOH+             3.455-08             2.560-08             7.408-01
      MGSO3             5.962-03             6.757-03             1.133+00
      MGSO4             5.964-02             6.760-02             1.133+00

      NA+               3.839-02             2.721-02             7.087-01
      NAOH              6.330-12             7.172-12             1.133+00
      NASO3-            8.272-05             6.128-05             7.408-01
      NASO4-            1.190-03             8.818-04             7.408-01

      OH-               1.322-07             9.791-08             7.408-01
      CL-               3.827-01             2.344-01             6.126-01





      SO3--             7.278-04             1.126-04             1.547-01
      SO4--             5.142-02             5.365-03             1.043-01

     COMPONENT          MOLALITY        ACTIVITY PRODUCT  RELATIVE SATURATION

      CA(OH)2(S)        0.000                3.872-17             1.143-11
      CASO3(S)          0.000                4.522-07             8.697+00
      CASO4(S)          0.000                2.118-05             9.539-01
      MG(OH)2(S)        0.000                4.832-16             5.081-05
      MGSO3(S)          0.000                5.479-06             9.325-02

     PSO2 = 1.65873-07  ATM.

                    MOLECULAR WATER = 1.00344+00 KGS.

                 IONIC STRENGTH = 7.15242-01        RES. E.N. =  -5.324-02
```

RUN NO. 47

DATE 2/3/76

$e^{-T/\tau}$ .066

ANALYTICAL RESULTS

Species	Standards (% Deviation)	Ca^+ Feed (mmole/l)	SO_3^{-2} Feed (mmole/l)	Effluent (mmole/l)	Solids (mmole/g)
Ca^{+2}	-.1	61.9	--	22.7	7.32
Mg^{+2}	0	--	694.	354	.03
Na_2^{+1}	-.8	6.7	40.5	22.7	.03
Cl^{-1}	.3	125.	106.	634	--
CO_3^{-2}	--	--	--	--	--
Ts^{-2}	1.0	--	230.	116.	6.63
SO_3^{-2}	--	--	33.4	12.9	6.38
SO_4^{-2}	1.0	--	197.	103.	1.07

OPERATING DATA

Time (min)	pH	Temp. (^oC)	SO_3^{-2} (mmole/l)	Solids Removal (ml/min)	Solids (wt%)	Solids (g)
20	6.20	48.5		47.5		
30	6.22	48.5	12.9	47.5	.17	5.5
90	6.22	49.0	13.4	49.0	.17	5.4
180	6.18	49.5	12.9	50.9	.19	6.2

COMPUTER RESULTS

Ionic Strength	Residual Electroneutrality	Relative Saturation			Mole Fraction	
		$CaSO_3\cdot\frac{1}{2}H_2O$	$CaSO_4\cdot 2H_2O$	$CaSO_4\cdot\frac{1}{2}H_2O$	SO_3^{-2}	SO_4^{-2}
1.03	-0.0642	6.21	0.61	0.26	.85	.15

REACTOR MATERIAL BALANCE CALCULATIONS

Run # 47 Date 2/3/76

INLET		A	B	Σ
Flow Rate (ml/min)		50	50	100
Ca^{+2}	(mmole/min)	3.10	--	3.10
Mg^{+2}	(mmole/min)	--	34.7	34.7
Na_2^{+2}	(mmole/min)	.3	2.03	2.37
Cl^{-1}	(mmole/min)	6.26	53.1	59.4
Ts	(mmole/min)	--	11.5	11.5
SO_3^{-2}	(mmole/min)	--	1.67	1.67
SO_4^{-2}	(mmole/min)	--	9.9	9.9

OUTLET		Liquid	Solid	Σ
Flow Rate (ml/min)		100	.096 (g/min)	
Ca^{+2}	(mmole/min)	2.27	.70	2.97
Mg^{+2}	(mmole/min)	35.4	.003	35.4
Na_2^{+2}	(mmole/min)	2.27	.003	2.27
Cl^{-1}	(mmole/min)	63.4	--	63.4
Ts	(mmole/min)	11.63	.67	12.3
SO_3^{-2}	(mmole/min)	1.29	.61	1.90
SO_4^{-2}	(mmole/min)	10.34	.10	10.4

PREC. RATE	mmole/min	mmole/g	grams/min
Solid			.096
Ca^{+2}	.83	7.11	.117
SO_3^{-2}	.38	6.38	.060
SO_4^{-2}	-.78	.59	-1.32

SOLIDS MATERIAL BALANCE

Run # 47 Date 2/03/76

	g/mmole	mmole/gram	g/gram
Ca^{+2}	.040	7.32	.293
Mg^{+2}	.024	.03	.001
Na_2^{+2}	.046	.03	.001
Cl^{-1}	.035	----	----
CO_3^{-2}	.060	----	----
SO_3^{-2}	.080	6.38	.511
SO_4^{-2}	.096	1.07	.103
$\frac{1}{2}H_2O$	.009	6.97	.063

Σ .972

KINETIC RUN 47

```
03 MAR 75     14:15:42.581                                  TEMPERATURE     49.500 DEG. C.
                                   INPUT SPECIES (MOLES)

                 H2O   = 5.55062+01                    HCL   = 6.34000-01
                 CAO   = 2.27000-02                    CO2   = 0.00000
                 MGO   = 3.54000-01                    N2O3  = 0.00000
                 NA2O  = 2.27000-02                    N2O5  = 0.00000
                                                       SO2   = 1.29000-02
                                                       SO3   = 1.23000-01

        PH =  6.2001


        SUPERSATURATION ALLOWED

                        AQUEOUS SOLUTION EQUILIBRIA

        COMPONENT          MOLALITY            ACTIVITY     ACTIVITY COEFFICIENT

         H+                5.733-07            6.308-07           1.100+00
         H2O                                                      9.824-01
         H2SO3             9.987-08            1.196-07           1.197+00
         HSO3-             2.455-03            1.497-03           6.098-01
         HSO4-             5.486-07            4.318-07           7.868-01

         CA++              1.812-02            4.141-03           2.285-01
         CAOH+             1.213-08            9.541-09           7.868-01
         CASO3             1.184-03            1.417-03           1.197+00
         CASO4             3.271-03            3.915-03           1.197+00

         MG++              2.857-01            8.257-02           2.891-01
         MGOH+             4.535-06            3.568-06           7.868-01
         MGSO3             8.361-03            1.001-02           1.197+00
         MGSO4             5.797-02            6.941-02           1.197+00

         NA+               4.424-02            3.156-02           7.133-01
         NAOH              5.882-12            7.043-12           1.197+00
         NASO3-            [illegible]         5.428-05           7.868-01
         NASO4-            8.156-04            6.425-04           7.868-01

         OH-               1.054-07            8.291-08           7.868-01
         CL-               6.304-01            3.764-01           5.971-01







         SO3--             7.409-04            1.018-04           1.374-01
         SO4--             4.035-02            3.362-03           8.332-02

        COMPONENT          MOLALITY       ACTIVITY PRODUCT   RELATIVE SATURATION

         CA(OH)2(S)        0.000               2.946-17           8.451-12
         CASO3(S)          0.000               4.179-07           6.278+00
         CASO4(S)          0.000               1.344-05           6.074-01
         MG(OH)2(S)        0.000               5.676-16           5.965-05
         MGSO3(S)          0.000               7.972-06           1.368-01

        PSO2 = 2.23562-07  ATM.

                      MOLECULAR WATER = 1.00569+00 KGS.

                    IONIC STRENGTH = 1.02876+00        RES. E.N. =  -6.417-02
```

RUN NO. 48

DATE 2/4/76

$e^{-T/\tau}$ <.01

ANALYTICAL RESULTS

Species	Standards (% Deviation)	Ca^{+} Feed (mmole/l)	SO_3^{-2} Feed (mmole/l)	Effluent (mmole/l)	Solids (mmole/g)
Ca^{+2}	-.1	65	--	30.8	7.06
Mg^{+2}	0	--	1060	520	.07
Na_2^{+1}	-.8	2.7	360	19.8	.03
Cl^{-1}	.3	130	1600	880	--
CO_3^{-2}	--	--	--	--	--
Ts^{-2}	1.0	--	214	95.7	6.98
SO_3^{-2}	--	--	27.8	10.3	5.97
SO_4^{-2}	1.0	--	186	85.4	1.16

OPERATING DATA

Time (min)	pH	Temp. (°C)	SO_3^{-2} (mmole/l)	Solids Removal (ml/min)	Solids (wt%)	Solids (g)
40	6.36	49	11.3			
120	6.27	50.2	11.0	24	.23	7.4
182	6.24	51.0	10.7	25.4	.22	7.4
310	6.27	50.6	10.4	46.8	.19	6.1
385	6.24	51.0	10.3	46.9	.16	5.1

COMPUTER RESULTS

Ionic Strength	Residual Electroneutrality	Relative Saturation			Mole Fraction	
		$CaSO_3 \cdot \frac{1}{2}H_2O$	$CaSO_4 \cdot 2H_2O$	$CaSO_4 \cdot \frac{1}{2}H_2O$	SO_3^{-2}	SO_4^{-2}
1.48	0.070	5.44	.54	.25	.84	.16

REACTOR MATERIAL BALANCE CALCULATIONS

Run # K-48 Date 2/4/76

INLET		A	B	Σ
Flow Rate (ml/min)		48.9	49.7	98.6
Ca^{+2}	(mmole/min)	3.18	--	3.18
Mg^{+2}	(mmole/min)	--	52.7	52.7
Na_2^{+2}	(mmole/min)	.13	1.79	1.92
Cl^{-1}	(mmole/min)	6.36	79.5	85.9
Ts	(mmole/min)	--	10.6	10.6
SO_3^{-2}	(mmole/min)	--	1.38	1.38
SO_4^{-2}	(mmole/min)	--	9.2	9.2

OUTLET		Liquid	Solid	Σ
Flow Rate (ml/min)		98.6	.074 (g/min)	
Ca^{+2}	(mmole/min)	3.04	.52	3.56
Mg^{+2}	(mmole/min)	51.3	--	51.3
Na_2^{+2}	(mmole/min)	1.95	--	1.95
Cl^{-1}	(mmole/min)	86.8	--	86.8
Ts	(mmole/min)	9.4	.52	9.92
SO_3^{-2}	(mmole/min)	1.02	.44	1.46
SO_4^{-2}	(mmole/min)	8.42	.09	8.53

PREC. RATE	mmole/min	mmole/g	grams/min
Solid			.074
Ca^{+2}	.14	7.06	.020
SO_3^{-2}	.36	5.97	.060
SO_4^{-2}	.78	1.16	.672

SOLIDS MATERIAL BALANCE

Run # 48 Date 2/4/76

	g/mmole	mmole/gram	g/gram
Ca^{+2}	.040	7.06	.282
Mg^{+2}	.024	.07	.002
Na_2^{+2}	.046	.03	.001
Cl^{-1}	.035	----	----
CO_3^{-2}	.060	----	----
SO_3^{-2}	.080	5.97	.478
SO_4^{-2}	.096	1.16	.111
$\frac{1}{2}H_2O$	.009	7.13	.064

Σ .938

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KINETIC RUN 48

```
03 MAR 76     14115144,874
                                                    TEMPERATURE     51,000 DEG, C.
                          INPUT SPECIES (MOLES)

              H2O  = 5,55682+01               HCL  = 8,80000-01
              CAO  = 3,48004-02               CO2  = 0,00000
              MGO  = 5,20000-01               N2O3 = 0,00000
              NA2O = 1,60000-02               N2O5 = 0,00000
                                              SO2  = 1,03200-02
                                              SO3  = 8,54000-02

      PH =  5,2470

      SUPERSATURATION ALLOWED

                    AQUEOUS SOLUTION EQUILIBRIA

      COMPONENT         MOLALITY            ACTIVITY       ACTIVITY COEFFICIENT

      H+                4,282-07            5,753-07            1,344+00
      H2O                                                       9,749-01
      H2SO3             4,376-04            5,668-04            1,295+00
      HSO3-             1,289-03            7,570-04            5,872-01
      HSO4-             2,019-07            2,371-07            8,742-01

      CA++              2,603-02            6,640-03            2,475-01
      CAOH+             2,085-08            1,836-08            8,792-01
      CASO3             9,000-04            1,255-03            1,295+00
      CASO4             2,784-03            3,563-03            1,295+00

      MG++              4,551-01            1,472-01            3,235-01
      MGOH+             8,753-08            7,696-08            8,792-01
      MGSO3             7,481-03            9,689-03            1,295+00
      MGSO4             5,326-02            6,902-02            1,295+00

      NA+               3,884-02            2,842-02            7,318-01
      NAOH              5,423-10            7,543-10            1,295+00
      NASO3-            3,574-05            3,142-05            8,792-01
      NASO4-            3,699-04            3,252-04            8,792-01

      OH-               1,171-07            9,802-08            3,792-01
      CL-               6,731-01            4,922-01            5,835-01




      SO3--             4,049-04            5,529-05            1,149-01
      SO4--             2,831-02            1,875-03            6,622-02
      COMPONENT         MOLALITY         ACTIVITY PRODUCT  RELATIVE SATURATION

      CA(OH)2(S)        0,000               6,455-17            1,998-11
      CASO3(S)          0,000               3,624-07            5,448+00
      CASO4(S)          0,000               1,163-05            5,413-01
      MG(OH)2(S)        0,000               1,431-15            1,536-04
      MGSO3(S)          0,000               7,542-06            1,336-01
      PSO2 = 1,11726-07  ATM.

                  MOLECULAR WATER = 1,00791+00 KGS.

                IONIC STRENGTH = 1,47834+00        RES. E.N. =   7,049-02
```

RUN NO. 49

DATE 2/10/76

$e^{-T/\tau}$ .24

ANALYTICAL RESULTS

Species	Standards (% Deviation)	Ca$^+$ Feed (mmole/l)	SO_3^{-2} Feed (mmole/l)	Effluent (mmole/l)	Solids (mmole/g)
Ca^{+2}	-.1	62	--	29.4	7.45
Mg^{+2}	0	--	940	500	.05
Na_2^{+1}	-.8	2.4	41.6	22.2	.03
Cl^{-1}	.3	126	1670.	853	--
CO_3^{-2}	--	--	--	--	--
Ts^{-2}	1.0	--	230	101	6.95
SO_3^{-2}	--	--	18.2	7.69	6.30
SO_4^{-2}	1.0	--	212	93	.95

OPERATING DATA

Time (min)	pH	Temp. (°C)	SO_3^{-2} (mmole/l)	Solids Removal (ml/min)	Solids (wt%)	Solids (g)
50	6.18	49.1	8.5	--	--	--
130	5.99	49.0	9.4	8.0	.138	4.5
200	6.00	50.0	9.5	8.0	.125	4.1
320	6.21	51.2	8.3	8.0	.153	5.0
410	6.19	51.1	8.30	7.9	.165	5.4
495	6.10	51.0	8.7	7.8	.202	6.6
583	6.20	50.9	8.0	7.8	.179	5.8
643	6.21	50.0	7.7	7.8	.201	6.5

COMPUTER RESULTS

Ionic Strength	Residual Electroneutrality	Relative Saturation			Mole Fraction	
		$CaSO_3\cdot\frac{1}{2}H_2O$	$CaSO_4\cdot 2H_2O$	$CaSO_4\cdot\frac{1}{2}H_2O$	SO_3^{-2}	SO_4^{-2}
1.43	.049	3.92	.57	.26	.85	.15

REACTOR MATERIAL BALANCE CALCULATIONS

Run # K-49 Date 2/10/76

INLET		A	B	Σ
Flow Rate (ml/min)		50.2	50.2	100.4
Ca^{+2}	(mmole/min)	3.11	--	3.11
Mg^{+2}	(mmole/min)	--	47.2	47.2
Na_2^{+2}	(mmole/min)	.12	2.09	2.21
Cl^{-1}	(mmole/min)	6.33	83.8	90.1
Ts	(mmole/min)	--	11.5	11.5
SO_3^{-2}	(mmole/min)	--	.91	.91
SO_4^{-2}	(mmole/min)	--	10.6	10.6

OUTLET		Liquid	Solid		Σ
Flow Rate (ml/min)		100.4	.0157	(g/min)	
Ca^{+2}	(mmole/min)	2.95	.117		3.07
Mg^{+2}	(mmole/min)	50.0	--		50.0
Na_2^{+2}	(mmole/min)	2.23	--		2.23
Cl^{-1}	(mmole/min)	88.4	--		88.4
Ts	(mmole/min)	10.1	.109		10.2
SO_3^{-2}	(mmole/min)	.77	.099		.87
SO_4^{-2}	(mmole/min)	9.35	.015		9.37

PREC. RATE	mmole/min	mmole/g	grams/min
Solid			.0157
Ca^{+2}	.16	7.45	.0215
SO_3^{-2}	.14	6.30	.0222
SO_4^{-2}	1.25	.95	1.32

SOLIDS MATERIAL BALANCE

Run # 49 Date 2/10/76

	g/mmole	mmole/gram	g/gram
Ca^{+2}	.040	7.45	.298
Mg^{+2}	.024	.05	.001
Na_2^{+2}	.046	.03	.001
Cl^{-1}	.035	--	--
CO_3^{-2}	.060	--	--
SO_3^{-2}	.080	6.30	.504
SO_4^{-2}	.096	.95	.091
$\frac{1}{2}H_2O$	.009	7.25	.065
		Σ	.961

KINETIC RUN 49

```
15 MAR 70    17:11:52.003                              TEMPERATURE    54.000 DEG. C.
                              INPUT SPECIES (MOLES)

                 H2O  = 5.55082+01              HCL  = 8.53000-01
                 CAO  = 2.94000-02              CO2  = 0.00000
                 MGO  = 5.00000-01              N2O3 = 0.00000
                 NA2O = 2.20000-02              N2O5 = 0.00000
                                                SO2  = 7.60000-03
                                                SO3  = 9.30000-02

         PH =  5.2101

         SUPERSATURATION ALLOWED

                      AQUEOUS SOLUTION EQUILIBRIA

         COMPONENT         MOLALITY           ACTIVITY     ACTIVITY COEFFICIENT

          H+                4.609-06          6.103-06          1.312+00
          H2O                                                   9.757-01
          H2SO3             3.821-08          4.879-08          1.284+00
          HSO3-             1.051-03          6.144-04          5.847-01
          HSO4-             3.137-07          2.720-07          8.672-01

          CA++              2.952-02          5.255-03          2.450-01
          CAOH+             1.746-08          1.514-08          8.672-01
          CASO3             7.053-04          9.053-04          1.284+00
          CASO4             2.947-03          3.783-03          1.284+00

          MG++              4.332-01          1.362-01          3.141-01
          MGOH+             7.254-08          6.291-08          8.672-01
          MGSO3             5.490-03          7.047-03          1.284+00
          MGSO4             5.747-02          7.379-02          1.284+00

          NA+               4.355-02          3.174-02          7.288-01
          NAOH              5.779-12          7.419-12          1.284+00
          NASO3-            3.135-05          2.719-05          8.672-01
          NASO4-            4.744-04          4.114-04          8.672-01

          OH-               1.001-08          8.683-09          8.672-01
          CL-               8.485-01          4.793-01          5.649-01




          SO3--             3.341-04          4.249-05          1.272-01
          SO4--             3.144-02          2.135-03          6.790-02

         COMPONENT         MOLALITY       ACTIVITY PRODUCT  RELATIVE SATURATION

          CA(OH)2(S)        0.000             4.716-17          1.421-11
          CASO3(S)          0.000             2.846-07          3.944+00
          CASO4(S)          0.000             1.271-05          5.769-01
          MG(OH)2(S)        0.000             1.042-15          1.187-04
          MGSO3(S)          0.000             5.490-05          9.539-02

          PSO2 = 6.32414-08  ATM.

                    MOLECULAR WATER = 1.00757+00 KGS.

                  IONIC STRENGTH = 1.42583+00        RES. E.N. =   4.040-22
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RUN NO. 50

DATE 2/17/76

$e^{-T/\tau}$ < .01

ANALYTICAL RESULTS

Species	Standards (mmoles/l)	Ca^{+} Feed (mmole/l)	SO_3^{-2} Feed (mmole/l)	Effluent (mmole/l)	Solids (mmole/g)
Ca^{+2}		36.9	----	9.53	7.36
Mg^{+2}		----	----	----	
Na_2^{+1}		----	43.1	20.2	
Cl^{-1}		74.8	----	43.3	
CO_3^{-2}		----	----	----	
Ts^{-2}		----	42.4	9.7	
SO_3^{-2}		----	20.8	1.90	7.00
SO_4^{-2}		----	21.6	7.8	.73

OPERATING DATA

Time (min)	pH	Temp. (°C)	SO_3^{-2} (mmole/l)	Solids Removal (ml/min)	Solids (wt%)	Solids (g)
58	7.95	40	1.90	400	0.102	2.79

COMPUTER RESULTS

Ionic Strength	Residual Electroneutrality	Relative Saturation			Mole Fraction	
		$CaSO_3 \cdot \frac{1}{2}H_2O$	$CaSO_4 \cdot 2H_2O$	$CaSO_4 \cdot \frac{1}{2}H_2O$	SO_3^{-2}	SO_4^{-2}
0.0677	-0.0032	6.6	0.25	0.09	0.91	0.09

REACTOR MATERIAL BALANCE CALCULATIONS

Run # 50 Date 2/17/76

INLET		A	B		Σ
Flow Rate (ml/min)		200	200		400
Ca^{+2}	(mmole/min)	7.38	----		7.38
Mg^{+2}	(mmole/min)	----	----		----
Na_2^{+2}	(mmole/min)	----	8.62		8.62
Cl^{-1}	(mmole/min)	15.0	----		15.0
Ts	(mmole/min)	----	8.48		8.48
SO_3^{-2}	(mmole/min)	----	4.16		4.16
SO_4^{-2}	(mmole/min)	----	4.32		4.32

OUTLET		Liquid	Solid		Σ
Flow Rate (ml/min)		400	.408	(g/min)	
Ca^{+2}	(mmole/min)	3.81	3.00		6.81
Mg^{+2}	(mmole/min)	----	----		----
Na_2^{+2}	(mmole/min)	8.08	----		8.08
Cl^{-1}	(mmole/min)	17.3	----		17.3
Ts	(mmole/min)	3.88	----		----
SO_3^{-2}	(mmole/min)	0.76	2.86		3.62
SO_4^{-2}	(mmole/min)	3.12	0.30		3.42

PREC. RATE	mmole/min	mmole/g	grams/min
Solid			0.408
Ca^{+2}	3.57	7.36	0.485
SO_3^{-2}	3.40	7.00	0.486
SO_4^{-2}	1.20	0.73	1.64

SOLIDS MATERIAL BALANCE

Run # 50 Date 2/17/76

	g/mmole	mmole/gram	g/gram
Ca^{+2}	.040	7.36	0.295
Mg^{+2}	.024		
Na_2^{+2}	.046		
Cl^{-1}	.035		
CO_3^{-2}	.060		
SO_3^{-2}	.080	7.00	.560
SO_4^{-2}	.096	.73	.070
$\frac{1}{2}H_2O$	.009	7.73	.070
			Σ 0.995

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KINETIC RUN 50

```
15 MAR 74    17:11:45.655                                   TEMPERATURE    40.002 DEG. C.
                                  INPUT SPECIES (MOLES)

                H2O  = 5.55062+01                  HCL  = 4.33002-02
                CAO  = 9.53400-03                  CO2  = 0.00000
                MGO  = 0.00000                     N2O3 = 0.00000
                NA2O = 2.22300-02                  N2O5 = 0.00000
                                                   SO2  = 1.97006-03
                                                   SO3  = 7.82000-03

          PH =  7.9524


          SUPERSATURATION ALLOWED

                          AQUEOUS SOLUTION EQUILIBRIA

         COMPONENT           MOLALITY            ACTIVITY      ACTIVITY COEFFICIENT

          H+                 1.330-08            1.122-08             8.436-01
          H2O                                                         9.984-01
          H2SO3              4.572-11            4.627-11             1.012+00
          HSO3-              4.908-05            3.911-05             7.969-01
          HSO4-              4.574-07            3.650-07             7.979-01

          CA++               6.674-03            2.775-03             4.158-01
          CAOH+              2.392-07            1.901-07             7.979-01
          CASO3              1.418-03            1.435-03             1.012+00
          CASO4              1.446-03            1.463-03             1.012+00

          NA+                3.984-02            3.225-02             8.096-01
          NAOH               2.243-09            2.270-09             1.012+00
          NASO3-             6.935-06            5.534-06             7.979-01
          NASO4-             4.992-04            3.983-04             7.979-01

          OH-                3.275-06            2.614-06             7.979-01
          CL-                4.328-02            3.424-02             7.911-01
          SO3--              4.253-04            1.715-04             4.033-01
          SO4--              5.652-03            2.149-03             3.803-01

         COMPONENT           MOLALITY        ACTIVITY PRODUCT  RELATIVE SATURATION







         CA(OH)2(S)          0.000               1.855-14             4.566-09
         CASO3(S)            0.000               4.758-07             6.595+00
         CASO4(S)            0.000               5.945-06             2.537-01

         PSO2 = 5.32772-11  ATM.

                         MOLECULAR WATER = 1.00239+00 KGS.

                       IONIC STRENGTH = 5.77294-02        RES. E.N. =  -3.195-03
```

RUN NO. 51

DATE 2/17/76

$e^{-T/\tau}$ < 0.01

ANALYTICAL RESULTS

Species	Standards (mmoles/l)	Ca^+ Feed (mmole/l)	SO_3^{-2} Feed (mmole/l)	Effluent (mmole/l)	Solids (mmole/g)
Ca^{+2}		36.9	----	9.02	7.34
Mg^{+2}		----	----	----	
Na_2^{+1}		----	43.1	20.5	
Cl^{-1}		74.8	----	41.0	
CO_3^{-2}		----	----	----	
Ts^{-2}		----	42.4	10.5	
SO_3^{-2}		----	20.8	1.84	6.70
SO_4^{-2}		----	21.6	8.7	.69

OPERATING DATA

Time (min)	pH	Temp. (°C)	SO_3^{-2} (mmole/l)	Solids Removal (ml/min)	Solids (wt%)	Solids (g)
68	8.70	41	1.84	200	0.101	2.77

COMPUTER RESULTS

Ionic Strength	Residual Electroneutrality	Relative Saturation			Mole Fraction	
		$CaSO_3\cdot\frac{1}{2}H_2O$	$CaSO_4\cdot 2H_2O$	$CaSO_4\cdot\frac{1}{2}H_2O$	SO_3^{-2}	SO_4^{-2}
0.0673	-0.0031	6.38	0.26	0.10	0.91	0.09

REACTOR MATERIAL BALANCE CALCULATIONS

Run # 51 Date 2/17/76

INLET		A	B	Σ
Flow Rate (ml/min)		100	100	200
Ca^{+2}	(mmole/min)	3.69	----	3.69
Mg^{+2}	(mmole/min)	----	----	----
Na_2^{+2}	(mmole/min)	----	4.31	4.31
Cl^{-1}	(mmole/min)	7.50	----	7.50
Ts	(mmole/min)	----	4.24	4.24
SO_3^{-2}	(mmole/min)	----	2.08	2.08
SO_4^{-2}	(mmole/min)	----	2.16	2.16

OUTLET		Liquid	Solid	Σ
Flow Rate (ml/min)		200	0.202 (g/min)	
Ca^{+2}	(mmole/min)	1.80	1.48	3.28
Mg^{+2}	(mmole/min)	----	----	----
Na_2^{+2}	(mmole/min)	4.10		4.10
Cl^{-1}	(mmole/min)	8.20		8.20
Ts	(mmole/min)	2.10	----	----
SO_3^{-2}	(mmole/min)	0.368	1.77	2.14
SO_4^{-2}	(mmole/min)	1.74	0.14	1.88

PREC. RATE	mmole/min	mmole/g	grams/min
Solid			0.202
Ca^{+2}	1.89	7.34	.257
SO_3^{-2}	1.71	6.70	.255
SO_4^{-2}	.42	.69	.61

SOLIDS MATERIAL BALANCE

Run # 51 Date 2/17/ 76

	g/mmole	mmole/gram	g/gram
Ca^{+2}	.040	7.34	0.294
Mg^{+2}	.024		
Na_2^{+2}	.046		
Cl^{-1}	.035		
CO_3^{-2}	.060		
SO_3^{-2}	.080	6.70	.536
SO_4^{-2}	.096	.69	.066
$\frac{1}{2}H_2O$	.009	7.39	.067
			Σ .963

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KINETIC RUN 51

```
15 MAR 74    17:11:49.868                                    TEMPERATURE    41.000 DEG. C.
                                  INPUT SPECIES (MOLES)

                    H2O  = 5.55062+01              HCL  = 4.19000-02
                    CAO  = 9.42000-03              CO2  = 0.00000
                    MGO  = 0.00000                 N2O3 = 0.00000
                    NA2O = 2.25000-02              N2O5 = 0.00000
                                                   SO2  = 1.54000-03
                                                   SO3  = 9.70000-03

          PH =  8.700

          SUPERSATURATION ALLOWED

                         AQUEOUS SOLUTION EQUILIBRIA

         COMPONENT         MOLALITY           ACTIVITY      ACTIVITY COEFFICIENT

          H+               2.379-09           1.995-09           8.395-01
          H2O                                                    9.964-01
          H2SO3            1.565-12           1.584-12           1.012+00
          HSO3-            9.283-06           7.362-06           7.909-01
          HSO4-            9.483-10           7.566-10           7.979-01

          CA++             5.110-03           2.544-03           4.168-01
          CAOH+            1.322-06           1.055-06           7.979-01
          CASO3            1.376-03           1.394-03           1.012+00
          CASO4            1.522-03           1.540-03           1.012+00

          NA+              4.041-02           3.206-02           7.936-01
          NAOH             1.364-07           1.380-07           1.012+00
          NASO3-           7.349-05           5.864-05           7.979-01
          NASO4-           5.742-04           4.582-04           7.979-01

          OH-              1.957-05           1.561-05           7.979-01
          CL-              4.094-02           3.243-02           7.912-01
          SO3--            4.447-04           1.794-04           4.034-01
          SO4--            6.591-03           2.425-03           3.674-01

         COMPONENT         MOLALITY       ACTIVITY PRODUCT   RELATIVE SATURATION




          CA(OH)2(S)       0.000              6.277-13           1.551-07
          CASO3(S)         0.000              4.569-07           6.382+00
          CASO4(S)         0.000              6.163-06           2.642-01

          PSO2 = 2.23684-12  ATM.

                         MOLECULAR WATER = 1.00037+00 KGS.

                       IONIC STRENGTH = 5.73223-02        RES. E.N. =  -3.053-03
```

RUN NO. 52

DATE 2/17/76

$e^{-T/\tau}$ <0.01

ANALYTICAL RESULTS

Species	Standards (mmoles/1)	Ca^{+} Feed (mmole/1)	SO_3^{-2} Feed (mmole/1)	Effluent (mmole/1)	Solids (mmole/g)
Ca^{+2}		36.9	----	9.01	7.51
Mg^{+2}		----	----	----	
Na_2^{+1}		----	43.1	21.4	
Cl^{-1}		74.8	----	40.6	
CO_3^{-2}			----	----	
Ts^{-2}			42.4	9.5	
SO_3^{-2}			20.8	1.59	6.22
SO_4^{-2}			21.6	7.9	.37

OPERATING DATA

Time (min)	pH	Temp. (°C)	SO_3^{-2} (mmole/1)	Solids Removal (ml/min)	Solids (wt%)	Solids (g)
83	8.11	49.1	1.59	200	0.097	2.67

COMPUTER RESULTS

Ionic Strength	Residual Electroneutrality	Relative Saturation			Mole Fraction	
		$CaSO_3 \cdot \frac{1}{2}H_2O$	$CaSO_4 \cdot 2H_2O$	$CaSO_4 \cdot \frac{1}{2}H_2O$	SO_3^{-2}	SO_4^{-2}
0.0666	0.0013	5.37	0.25	0.11	0.89	0.11

REACTOR MATERIAL BALANCE CALCULATIONS

Run # 52 Date 2/12/76

INLET		A	B	Σ
Flow Rate (ml/min)		100	100	200
Ca^{+2}	(mmole/min)	3.69	----	3.69
Mg^{+2}	(mmole/min)	----	----	----
Na_2^{+2}	(mmole/min)	----	4.31	4.31
Cl^{-1}	(mmole/min)	7.48	----	7.48
Ts	(mmole/min)	----	4.24	4.24
SO_3^{-2}	(mmole/min)	----	2.08	2.08
SO_4^{-2}	(mmole/min)	----	2.16	2.16

OUTLET		Liquid	Solid	Σ
Flow Rate (ml/min)		200	0.194 (g/min)	
Ca^{+2}	(mmole/min)	1.80	1.46	3.26
Mg^{+2}	(mmole/min)	----	----	----
Na_2^{+2}	(mmole/min)	4.28	----	4.28
Cl^{-1}	(mmole/min)	8.12	----	8.12
Ts	(mmole/min)	1.90	----	---
SO_3^{-2}	(mmole/min)	.32	1.28	1.60
SO_4^{-2}	(mmole/min)	1.58	.02	1.60

PREC. RATE	mmole/min	mmole/g	grams/min
Solid			0.194
Ca^{+2}	1.89	7.51	.252
SO_3^{-2}	1.76	6.62	.266
SO_4^{-2}	.58	.37	1.57

SOLIDS MATERIAL BALANCE

Run # 52 Date 2/17/76

	g/mmole	mmole/gram	g/gram
Ca^{+2}	.040	7.51	0.301
Mg^{+2}	.024		
Na_2^{+2}	.046		
Cl^{-1}	.035		
CO_3^{-2}	.060		
SO_3^{-2}	.080	6.62	.530
SO_4^{-2}	.096	.80	.077
$\frac{1}{2}H_2O$	.009	6.99	.063
			Σ 0.971

KINETIC RUN 52

```
15 MAR 78    17111147,419                                    TEMPERATURE    49.100 DEG. C.
                                   INPUT SPECIES (MOLES)

               H2O  = 5.55082+01                   HCL  = 4.30000-02
               CAO  = 9.01075-03                   CO2  = 0.00000
               MGO  = 0.00000                      N2O3 = 0.00000
               NA2O = 2.14000-02                   N2O5 = 0.00000
                                                   SO2  = 1.59170-03
                                                   SO3  = 7.30000-03

          PH =  8.1100

          SUPERSATURATION ALLOWED

                           AQUEOUS SOLUTION EQUILIBRIA

         COMPONENT          MOLALITY           ACTIVITY      ACTIVITY COEFFICIENT

          H+                9.285-09           7.762-09           8.377-01
          H2O                                                     9.994-01
          H2SO3             2.428-11           2.458-11           1.012+00
          HSO3-             3.169-05           2.519-05           7.944-01
          HSO4-             4.192-09           3.343-09           7.957-01

          CA++              6.260-03           2.594-03           4.125-01
          CAOH+             6.243-07           4.968-07           7.957-01
          CASO3             1.201-03           1.215-03           1.012+00
          CASO4             1.516-03           1.535-03           1.012+00

          NA+               4.203-02           3.428-02           8.278-01
          NAOH              6.062-08           6.133-08           1.012+00
          NASO3-            5.996-06           4.771-06           7.957-01
          NASO4-            5.485-04           4.368-04           7.957-01

          OH-               8.423-06           6.687-06           7.957-01
          CL-               4.695-02           3.292-02           7.890-01
          SO3--             3.507-04           1.403-04           3.992-01
          SO4--             5.632-03           2.118-03           3.832-01
         COMPONENT          MOLALITY       ACTIVITY PRODUCT  RELATIVE SATURATION




          CA(OH)2(S)        0.000              1.102-13           3.424-06
          CASO3(S)          0.000              3.628-07           5.374+00
          CASO4(S)          0.000              5.475-06           2.468-01

          PSO2 = 4.26458-11  ATM.

                          MOLECULAR WATER = 1.00036+00 KGS.

                         IONIC STRENGTH = 6.66437-02        RES. E.R. =   1.269-03
```

RUN NO. 53

DATE 2/17/76

$e^{-T/\tau}$ <0.01

ANALYTICAL RESULTS

Species	Standards (mmoles/l)	Ca^{+} Feed (mmole/l)	SO_3^{-2} Feed (mmole/l)	Effluent (mmole/l)	Solids (mmole/g)
Ca^{+2}		36.9	----	6.92	7.40
Mg^{+2}		----	----	----	
Na_2^{+1}		----	43.1	21.8	
Cl^{-1}		74.8	----	39.6	
CO_3^{-2}		----	----	----	
Ts^{-2}		----	42.4	11.1	
SO_3^{-2}		----	20.8	1.44	6.69
SO_4^{-2}		----	21.6	9.66	.84

OPERATING DATA

Time (min)	pH	Temp. (°C)	SO_3^{-2} (mmole/l)	Solids Removal (ml/min)	Solids (wt%)	Solids (g)
65	8.30	61.4	1.44	200	0.125	3.44

COMPUTER RESULTS

Ionic Strength	Residual Electroneutrality	Relative Saturation			Mole Fraction	
		$CaSO_3 \cdot \frac{1}{2}H_2O$	$CaSO_4 \cdot 2H_2O$	$CaSO_4 \cdot \frac{1}{2}H_2O$	SO_3^{-2}	SO_4^{-2}
0.0658	-0.0044	4.33	0.23	0.13	0.89	0.11

REACTOR MATERIAL BALANCE CALCULATIONS

Run # 53 Date 2/17/76

INLET		A	B	Σ
Flow Rate (ml/min)		100	100	200
Ca^{+2}	(mmole/min)	3.69	----	3.69
Mg^{+2}	(mmole/min)	----	----	----
Na_2^{+2}	(mmole/min)	----	4.31	4.31
Cl^{-1}	(mmole/min)	7.48	----	7.48
Ts	(mmole/min)	----	4.24	4.24
SO_3^{-2}	(mmole/min)		2.08	2.08
SO_4^{-2}	(mmole/min)		2.16	2.16

OUTLET		Liquid	Solid	Σ
Flow Rate (ml/min)		200	0.250 (g/min)	
Ca^{+2}	(mmole/min)	1.38	1.88	3.26
Mg^{+2}	(mmole/min)	----	----	----
Na_2^{+2}	(mmole/min)	4.28	----	4.28
Cl^{-1}	(mmole/min)	7.92	----	7.92
Ts	(mmole/min)	2.22	1.88	4.10
SO_3^{-2}	(mmole/min)	0.29	1.67	1.96
SO_4^{-2}	(mmole/min)	1.93	0.21	2.14

PREC. RATE	mmole/min	mmole/g	grams/min
Solid			0.250
Ca^{+2}	2.31	7.40	.312
SO_3^{-2}	1.79	6.69	.268
SO_4^{-2}	.23	.84	.274

SOLIDS MATERIAL BALANCE

Run # 53 Date 2/17/76

	g/mmole	mmole/gram	g/gram
Ca^{+2}	.040	7.40	0.297
Mg^{+2}	.024		
Na_2^{+2}	.046		
Cl^{-1}	.035		
CO_3^{-2}	.060		
SO_3^{-2}	.080	6.69	.535
SO_4^{-2}	.096	.84	.081
$\frac{1}{2}H_2O$	.009	7.53	.068
			Σ .981

KINETIC RUN 53

```
15 MAR 76    17111146.101                                  TEMPERATURE    51.400 DEG. C.
                              INPUT SPECIES (MOLES)

               H2O  = 5.55062+01                 HCL  = 3.96000-02
               CAO  = 5.92000-03                 CO2  = 0.00000
               MGO  = 0.00000                    N2O3 = 0.00000
               NA2O = 2.16000-02                 N2O5 = 0.00000
                                                 SO2  = 1.44224-03
                                                 SO3  = 9.56000-03

        PH =  8.3000


        SUPERSATURATION ALLOWED

                       AQUEOUS SOLUTION EQUILIBRIA

       COMPONENT         MOLALITY          ACTIVITY       ACTIVITY COEFFICIENT

        H+               6.005-09          5.011-09           8.345-01
        H2O                                                   9.984-01
        H2SO3            1.526-11          1.546-11           1.012+00
        HSO3-            2.849-05          2.255-05           7.911-01
        HSO4-            4.933-09          3.906-09           7.918-01

        CA++             4.353-03          1.763-03           4.049-01
        CAOH+            1.371-06          1.085-06           7.918-01
        CASO3            1.017-03          1.028-03           1.012+00
        CASO4            1.547-03          1.565-03           1.012+00

        NA+              4.284-02          3.442-02           8.034-01
        NAOH             1.893-07          1.915-07           1.012+00
        NASO3-           6.637-06          5.255-06           7.918-01
        NASO4-           7.340-04          5.812-04           7.918-01

        OH-              2.611-05          2.067-05           7.918-01
        CL-              3.959-02          3.108-02           7.851-01
        SO3--            3.899-04          1.527-04           3.916-01
        SO4--            7.376-03          2.623-03           3.556-01

       COMPONENT         MOLALITY      ACTIVITY PRODUCT   RELATIVE SATURATION








        CA(OH)2(S)       0.000             7.534-13           2.955-07
        CASO3(S)         0.000             2.689-07           4.331+00
        CASO4(S)         0.000             4.668-06           2.330-01

        PSO2 = 4.26851-11  ATM.

                       MOLECULAR WATER = 1.00036+00 KGS.

                    IONIC STRENGTH = 6.58482-02        RES. E.N. =  -4.352-03
```

RUN NO. 56

DATE 2/24/76

$e^{-T/\tau}$ 0.018

ANALYTICAL RESULTS

Species	Standards (mmoles/l)	Ca^+ Feed (mmole/l)	SO_3^{-2} Feed (mmole/l)	Effluent (mmole/l)	Solids (mmole/g)
Ca^{+2}		43.2	----	14.7	7.39
Mg^{+2}		----	----	----	
Na_2^{+1}		----	42.8	21.0	
Cl^{-1}		80.	----	44.2	
CO_3^{-2}		----	----	----	
Ts^{-2}		----	40.3	10.8	
SO_3^{-2}		----	22.3	2.08	6.72
SO_4^{-2}		----	18.0	8.8	0.62

OPERATING DATA

Time (min)	pH	Temp. (°C)	SO_3^{-2} (mmole/l)	Solids Removal (ml/min)	Solids (wt%)	Solids (g)
				200		
				200		
55	828	4.10	2.08	200	0.115	3.16

COMPUTER RESULTS

Ionic Strength	Residual Electroneutrality	Relative Saturation			Mole Fraction	
		$CaSO_3 \cdot \frac{1}{2}H_2O$	$CaSO_4 \cdot 2H_2O$	$CaSO_4 \cdot \frac{1}{2}H_2O$	SO_3^{-2}	SO_4^{-2}
0.0774	0.0054	7.94	0.39	0.14	0.91	0.09

REACTOR MATERIAL BALANCE CALCULATIONS

Run # 56 Date 2/24/76

INLET	A	B	Σ
Flow Rate (ml/min)	100	100	200
Ca^{+2} (mmole/min)	4.32	----	4.32
Mg^{+2} (mmole/min)	----	----	----
Na_2^{+2} (mmole/min)	----	4.28	4.28
Cl^{-1} (mmole/min)	8.00	----	8.00
Ts (mmole/min)	----	4.03	4.03
SO_3^{-2} (mmole/min)	----	2.23	2.23
SO_4^{-2} (mmole/min)	----	1.80	1.80

OUTLET	Liquid	Solid	Σ
Flow Rate (ml/min)	200	0.230 (g/min)	
Ca^{+2} (mmole/min)	2.94	1.70	4.64
Mg^{+2} (mmole/min)		----	----
Na_2^{+2} (mmole/min)	4.20	----	4.20
Cl^{-1} (mmole/min)	8.84		8.84
Ts (mmole/min)	2.16	1.69	3.85
SO_3^{-2} (mmole/min)	.416	1.55	1.97
SO_4^{-2} (mmole/min)	1.76	0.14	1.90

PREC. RATE	mmole/min	mmole/g	grams/min
Solid			0.230
Ca^{+2}	1.36	7.39	.184
SO_3^{-2}	1.81	6.72	.270
SO_4^{-2}	0.04	.62	.065

SOLIDS MATERIAL BALANCE

Run # 56 Date 2/24/76

	g/mmole	mmole/gram	g/gram
Ca^{+2}	.040	7.39	0.296
Mg^{+2}	.024		
$Na_2{}^{+2}$	.046		
Cl^{-1}	.035		
$CO_3{}^{-2}$	.060		
$SO_3{}^{-2}$	.080	6.72	.538
$SO_4{}^{-2}$	.096	.62	.060
$\frac{1}{2}H_2O$	.009	7.34	.066

Σ 0.960

KINETIC RUN 56

```
15 MAR 79    17:11:49.754                                    TEMPERATURE    41.020 DEG. C.
                          INPUT SPECIES (MOLES)

              H2O  = 5.55062+01                 HCL  = 4.42034-02
              CAO  = 1.47392-02                 CO2  = 0.00000
              MGO  = 0.00000                    N2O3 = 0.00000
              NA2O = 2.14922-02                 N2O5 = 0.00000
                                                SO2  = 2.38040-03
                                                SO3  = 4.80702-03

       PH =  8.280


       SUPERSATURATION ALLOWED

                   AQUEOUS SOLUTION EQUILIBRIA

      COMPONENT          MOLALITY             ACTIVITY      ACTIVITY COEFFICIENT

        H+               6.280-09             5.247-09            8.356-01
        H2O                                                       9.963-01
        H2SO3            7.572-12             8.061-12            1.014+00
        HSO3-            1.817-05             1.432-05            7.878-01
        HSO4-            2.184-09             1.724-09            7.894-01

        CA++             1.075-02             4.302-03            3.990-01
        CAOH+            8.566-07             6.765-07            7.896-01
        CASO3            1.712-03             1.735-03            1.014+00
        CASO4            2.224-03             2.255-03            1.014+00

        NA+              4.146-02             3.322-02            8.013-01
        NAOH             5.262-08             5.334-08            1.014+00
        NASO3-           5.556-06             4.395-06            7.898-01
        NASO4-           5.118-04             4.041-04            7.896-01

        OH-              7.555-06             5.965-06            7.896-01
        CL-              4.418-02             3.453-02            7.815-01
        SO3--            3.434-04             1.323-04            3.852-01
        SO4--            6.262-03             2.175-03            3.473-01

      COMPONENT          MOLALITY         ACTIVITY PRODUCT  RELATIVE SATURATION







        CA(OH)2(S)       0.000                1.531-13            3.782-08
        CASO3(S)         0.000                5.606-07            7.041+00
        CASO4(S)         0.000                9.322-06            3.858-01

        PSO2 = 1.14124-11  ATM.

                    MOLECULAR WATER = 1.00040+00 KGS.

                  IONIC STRENGTH = 7.74156-02        RES. E.N. =   5.446-03
```

REACTOR MATERIAL BALANCE CALCULATIONS

Run # 59　　　　Date 3/10/76

INLET		A	B	Σ
Flow Rate (ml/min)		200	100	300
Ca^{+2}	(mmole/min)	4.12	----	4.12
Mg^{+2}	(mmole/min)			----
Na_2^{+2}	(mmole/min)	1.60	5.27	6.87
Cl^{-1}	(mmole/min)			----
Ts	(mmole/min)		9.72	9.72
SO_3^{-2}	(mmole/min)		4.07	4.07
SO_4^{-2}	(mmole/min)		5.65	5.65

OUTLET		Liquid	Solid	Σ
Flow Rate (ml/min)		300	0.0311 (g/min)	
Ca^{+2}	(mmole/min)	2.38	0.28	2.66
Mg^{+2}	(mmole/min)	---	---	---
Na_2^{+2}	(mmole/min)	6.84		6.84
Cl^{-1}	(mmole/min)	----		
Ts	(mmole/min)	7.11	0.051	7.16
SO_3^{-2}	(mmole/min)	2.78	0.047	2.83
SO_4^{-2}	(mmole/min)	4.32	0.004	4.32

PREC. RATE	mmole/min	mmole/g	grams/min
Solid			0.0311
Ca^{+2}	2.74	8.97	.305
SO_3^{-2}	1.29	1.50	.86
SO_4^{-2}	1.33	0.14	9.5

SOLIDS MATERIAL BALANCE

Run No. 59

Date 3/10/76

	g/mmole	mmole/gram	g/gram
Ca^{++}	0.040	8.97	0.359
Mg^{++}	.024		
Na_2^{++}	.046		
Cl^-	.035		
$CO_3^=$	.060	(7.33)*	(.440)*
$SO_3^=$	.080	1.50	.120
$SO_4^=$	.096	.14	.013
$\frac{1}{2}H_2O$	.009	1.64	.015
			Σ .947

---

* Excess calcium ([Ca] - [Ts]) is assumed to be calcium carbonate.

RUN NO. 59

DATE 3/10/76

$e^{-T/\tau}$ .57

ANALYTICAL RESULTS

Species	Standards (mmoles/l)	Ca^{+} Feed (mmole/l)	SO_3^{-2} Feed (mmole/l)	Effluent (mmole/l)	Solids (mmole/g)
Ca^{+2}		20.6		7.92	8.97
Mg^{+2}					
Na_2^{+1}		8.0	52.7	22.8	
Cl^{-1}					
CO_3^{-2}				5.2	
Ts^{-2}			97.2	23.7	1.45
SO_3^{-2}			40.7	9.25	1.50
SO_4^{-2}			56.5	14.4	.14

OPERATING DATA

Time (min)	pH	Temp. (°C)	SO_3^{-2} (mmole/l)	Solids Removal (ml/min)	Solids (wt%)	Solids (g)
60	5.45	45	13.4	10		
120	5.85	50	13.8			
152	6.15	52				
150	6.25	54	9.25	10	0.311	10.11

COMPUTER RESULTS

Ionic Strength	Residual Electroneutrality	Relative Saturation			Mole Fractio	
		$CaSO_3\cdot\frac{1}{2}H_2O$	$CaSO_4\cdot 2H_2O$	$CaSO_4\cdot\frac{1}{2}H_2O$	SO_3^{-2}	SO_4^{-2}
0.0584	0.0170	7.87	0.31	0.15	0.82	0.18

KINETIC RUN 59

```
03 MAY 75    15:12:00,741                                   TEMPERATURE    54,000 DEG, C,
                              INPUT SPECIES (MOLES)

                  H2O  = 5,55062+01               HCL  = 0,00000
                  CAO  = 7,92000-03               CO2  = 5,20000-03
                  MGO  = 0,00000                  N2O3 = 0,00000
                  NA2O = 2,25000-02               N2O5 = 0,00000
                                                  SO2  = 9,26000-03
                                                  SO3  = 1,44000-02

              PH =  6,2500

              SUPERSATURATION ALLOWED

                           AQUEOUS SOLUTION EQUILIBRIA

              COMPONENT          MOLALITY          ACTIVITY     ACTIVITY COEFFICIENT

               H+                6,690-07          5,623-07          8,405-01
               H2O                                                   9,988-01
               H2CO3             2,341-03          2,365-03          1,010+00
               HCO3-             2,694-03          2,157-03          8,017-01
               H2SO3             3,583-07          3,620-07          1,010+00
               HSO3-             5,840-03          4,682-03          8,017-01
               HSO4-             7,034-07          5,641-07          8,019-01

               CA++              3,596-03          1,530-03          4,254-01
               CAOH+             6,693-09          5,367-09          8,019-01
               CAHCO3+           9,198-05          7,377-05          8,019-01
               CACO3             8,902-07          8,994-07          1,010+00
               CASO3             1,795-03          1,814-03          1,010+00
               CAHSO3+           4,874-04          3,909-04          8,019-01
               CASO4             1,949-03          1,969-03          1,010+00

               NA+               4,344-02          3,530-02          8,128-01
               NAOH              1,156-09          1,168-09          1,010+00
               NAHCO3            7,426-05          7,502-05          1,010+00
               NACO3-            1,159-06          9,297-07          8,019-01
               NASO3-            3,257-04          2,612-04          8,019-01
               NASO4-            1,167-03          9,359-04          8,019-01




               OH-               1,533-07          1,229-07          8,019-01
               CO3--             6,474-07          2,675-07          4,132-01
               SO3--             8,124-04          3,357-04          4,132-01
               SO4--             1,126-02          4,276-03          3,789-01

              COMPONENT          MOLALITY      ACTIVITY PRODUCT  RELATIVE SATURATION

               CA(OH)2(S)        0,000             2,311-17          7,027-12
               CACO3(S)          0,000             4,092-10          2,018-01
               CASO3(S)          0,000             5,132-07          7,865+00
               CASO4(S)          0,000             6,526-06          3,063-01

               PCO2 = 1,30672-01  ATM,
               PSO2 = 7,51601-07  ATM,

                           MOLECULAR WATER = 9,99875-01 KGS,

                         IONIC STRENGTH = 5,84093-02       RES, E,N, =   1,699-02
```

RUN NO. 60

DATE 3/11/76

$e^{-T/\tau}$ 0.07

ANALYTICAL RESULTS

Species	Standards (mmoles/l)	Ca^+ Feed (mmole/l)	SO_3^{-2} Feed (mmole/l)	Effluent (mmole/l)	Solids (mmole/g)
Ca^{+2}		22.8		4.24	7.54
Mg^{+2}					
Na_2^{+1}			72.9	38.7	
Cl^{-1}					
CO_3^{-2}				10.8	
Ts^{-2}			82.8	33.3	6.00
SO_3^{-2}			49.3	18.9	5.58
SO_4^{-2}			33.6	14.4	0.52

OPERATING DATA

Time (min)	pH	Temp. (°C)	SO_3^{-2} (mmole/l)	Solids Removal (ml/min)	Solids (wt%)	Solids (g)
30	5.62	53		36		
60	5.76	54		48	0.1882	6.12
120				32	.1877	6.10
200	5.66	54.2		31		
300	5.70	55		32	.1876	6.10

COMPUTER RESULTS

Ionic Strength	Residual Electroneutrality	Relative Saturation			Mole Fraction	
		$CaSO_3 \cdot \frac{1}{2}H_2O$	$CaSO_4 \cdot 2H_2O$	$CaSO_4 \cdot \frac{1}{2}H_2O$	SO_3^{-2}	SO_4^{-2}
0.0771	0.0336	2.98	0.14	0.07	0.88	0.12

REACTOR MATERIAL BALANCE CALCULATIONS

Run # 60 Date 3/11/76

INLET		A	B	Σ
Flow Rate (ml/min)		0.100	0.100	0.200
Ca^{+2}	(mmole/min)	2.28		2.28
Mg^{+2}	(mmole/min)			
Na_2^{+2}	(mmole/min)	0.50	7.29	7.79
Cl^{-1}	(mmole/min)			
Ts	(mmole/min)		8.28	8.28
SO_3^{-2}	(mmole/min)		4.93	4.93
SO_4^{-2}	(mmole/min)		3.36	3.36

OUTLET		Liquid	Solid	Σ
Flow Rate (ml/min)		0.200	0.195 (g/min)	
Ca^{+2}	(mmole/min)	0.85	1.47	2.32
Mg^{+2}	(mmole/min)			
Na_2^{+2}	(mmole/min)	7.74		7.74
Cl^{-1}	(mmole/min)			
Ts	(mmole/min)	6.66	1.19	7.85
SO_3^{-2}	(mmole/min)	3.78	1.09	4.87
SO_4^{-2}	(mmole/min)	2.88	0.10	2.98

PREC. RATE	mmole/min	mmole/g	grams/min
Solid			0.195
Ca^{+2}	1.43	7.54	0.190
SO_3^{-2}	1.15	5.58	.206
SO_4^{-2}	0.48	0.52	.92

SOLIDS MATERIAL BALANCE

Run No. 60

Date 3/11/76

	g/mmole	mmole/gram	g/gram
Ca^{++}	0.040	7.54	0.302
Mg^{++}	.024		
Na_2^{++}	.046		
Cl^-	.035		
$CO_3^=$	.060	(1.44)*	(.086)*
$SO_3^=$	.080	5.58	.446
$SO_4^=$	.096	.52	.050
$\frac{1}{2}H_2O$	.009	6.10	.055
			Σ .939

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* Excess calcium ([Ca] - [Ts]) is assumed to be calcium carbonate.

KINETIC RUN 60

```
03 MAY 76    16:12:02.512                                         TEMPERATURE    55.000 DEG. C.
                                   INPUT SPECIES (MOLES)

                    H2O  = 5.55082+01               HCL  = 0.00000
                    CAO  = 4.24400-03               CO2  = 1.05800-02
                    MGO  = 0.00000                  N2O3 = 0.00000
                    NA2O = 3.87000-02               N2O5 = 0.00000
                                                    SO2  = 1.89000-02
                                                    SO3  = 1.44000-02

            PH =  5.700

            SUPERSATURATION ALLOWED

                            AQUEOUS SOLUTION EQUILIBRIA

           COMPONENT          MOLALITY           ACTIVITY      ACTIVITY COEFFICIENT

            H+                2.398-06           1.945-06             8.318-01
            H2O                                                       9.980-01
            H2CO3             7.986-03           8.094-03             1.014+00
            HCO3-             2.658-03           2.075-03             7.830-01
            H2SO3             3.542-06           3.590-06             1.014+00
            HSO3-             1.641-02           1.285-02             7.830-01
            HSO4-             2.421-06           1.900-06             7.847-01

            CA++              1.931-03           7.545-04             3.906-01
            CAOH+             1.011-09           7.935-10             7.847-01
            CAHCO3+           4.489-05           3.523-05             7.847-01
            CACO3             1.208-07           1.224-07             1.014+00
            CASO3             6.006-04           6.001-04             1.014+00
            CAHSO3+           6.898-04           5.437-04             7.847-01
            CASO4             8.947-04           9.069-04             1.014+00

            NA+               7.500-02           5.976-02             7.967-01
            NAOH              5.812-10           5.891-10             1.014+00
            NAHCO3            1.205-04           1.222-04             1.014+00
            NACO3-            5.514-07           4.327-07             7.847-01
            NASO3-            4.351-04           3.414-04             7.847-01
            NASO4-            1.866-03           1.464-03             7.847-01




            OH-               4.668-08           3.663-08             7.847-01
            CO3--             1.944-07           7.306-08             3.759-01
            SO3--             6.816-04           2.562-04             3.759-01
            SO4--             1.164-02           3.932-03             3.377-01
           COMPONENT          MOLALITY         ACTIVITY PRODUCT  RELATIVE SATURATION

            CA(OH)2(S)        0.000              1.012-18             3.419-13
            CACO3(S)          0.000              5.512-11             3.655-02
            CASO3(S)          0.000              1.931-07             2.979+00
            CASO4(S)          0.000              2.955-06             1.399-01

            PCO2 = 4.55345-01  ATM.
            PSO2 = 7.78471-08  ATM.

                          MOLECULAR WATER = 9.99677-01 KGS.

                        IONIC STRENGTH = 7.78614-02        RES. E.N. =   3.358-02
```

RUN NO. 61

$e^{-T/\tau}$ 135

DATE 3/19/76

ANALYTICAL RESULTS

Species	Standards (mmoles/l)	Ca^+ Feed (mmole/l)	SO_3^{-2} Feed (mmole/l)	Effluent (mmole/l)	Solids (mmole/g)
Ca^{+2}		10.8		3.4	8.61
Mg^{+2}					
Na_2^{+1}			150	35.2	
Cl^{-1}					
CO_3^{-2}		10.8		9.4	
Ts^{-2}			27.4	44.2	
SO_3^{-2}			9.4	20.5	5.1
SO_4^{-2}			180.	23.7	0.40

OPERATING DATA

Time (min)	pH	Temp. (°C)	SO_3^{-2} (mmole/l)	Solids Removal (ml/min)	Solids (wt%)	Solids (g)
50	5.86	55.9	22.6	35	0.48	15.5
120	6.00	58.2	21.9	20	.34	11.1
165	6.10	55.8	22.1	20	.33	10.8
280	6.23	56.2	20.5	20	.27	8.9

COMPUTER RESULTS

Ionic Strength	Residual Electroneutrality	Relative Saturation			Mole Fraction	
		$CaSO_3 \cdot \frac{1}{2}H_2O$	$CaSO_4 \cdot 2H_2O$	$CaSO_4 \cdot \frac{1}{2}H_2O$	SO_3^{-2}	SO_4^{-2}
0.09	0.005	2.19	0.152	0.076	0.92	0.08

REACTOR MATERIAL BALANCE CALCULATIONS

Run # 61 Date 3/19/76

INLET		A	B	Σ
Flow Rate (ml/min)		150	50	200
Ca^{+2}	(mmole/min)	1.62	---	1.62
Mg^{+2}	(mmole/min)			
Na_2^{+2}	(mmole/min)		7.50	7.5
Cl^{-1}	(mmole/min)			
CO_3^{-2}	(mmole/min)	1.62		1.62
SO_3^{-2}	(mmole/min)		4.445	4.445
SO_4^{-2}	(mmole/min)		9.26	9.26

OUTLET		Liquid	Solid		Σ
Flow Rate (ml/min)		200	0.054	(g/min)	
Ca^{+2}	(mmole/min)	0.68	0.47		1.15
Mg^{+2}	(mmole/min)				
Na_2^{+2}	(mmole/min)	7.05			7.05
Cl^{-1}	(mmole/min)				
CO_3^{-2}	(mmole/min)	1.88	0.17		2.05
SO_3^{-2}	(mmole/min)	4.1	0.28		4.38
SO_4^{-2}	(mmole/min)	4.74	0.02		4.76

PREC. RATE	mmole/min	mmole/g	grams/min
Solid			0.054
Ca^{+2}	0.94	8.61	0.109
SO_3^{-2}	0.345	4.91	.070
SO_4^{-2}	4.52	0.44	10.3

SOLIDS MATERIAL BALANCE

Run No. 61

Date 3/19/76

	g/mmole	mmole/gram	g/gram
Ca^{++}	0.040	8.61	0.344
Mg^{++}	.024		
Na_2^{++}	.046		
Cl^-	.035		
$CO_3^=$	.060	(2.59)*	(0.155)*
$SO_3^=$	.080	5.50	.440
$SO_4^=$	.096	.52	.050
$\frac{1}{2}H_2O$	.009	6.02	.054
			Σ 1.043

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* Excess calcium ([Ca] - [Ts]) is assumed to be calcium carbonate.

KINETIC RUN 61

```
03 MAY 76    16:12:03,422                                        TEMPERATURE    55,000 DEG. C.
                                  INPUT SPECIES (MOLES)

                  H2O  = 5,55062+01                 HCL  = 0,00000
                  CAO  = 3,40000-03                 CO2  = 9,40000-03
                  MGO  = 0,00000                    N2O3 = 0,00000
                  NA2O = 3,52000-02                 N2O5 = 0,00000
                                                    SO2  = 2,05000-02
                                                    SO3  = 2,37000-02

           PH =  5,7000

           SUPERSATURATION ALLOWED

                      AQUEOUS SOLUTION EQUILIBRIA

          COMPONENT          MOLALITY             ACTIVITY     ACTIVITY COEFFICIENT

           H+                2,411-06             1,995-06          8,276-01
           H2O                                                      9,989-01
           H2CO3             6,946-03             7,056-03          1,016+00
           HCO3-             2,338-03             1,805-03          7,720-01
           H2SO3             3,934-06             3,997-06          1,016+00
           HSO3-             1,827-02             1,410-02          7,720-01
           HSO4-             4,035-06             3,127-06          7,750-01

           CA++              1,369-03             5,089-04          3,717-01
           CAOH+             7,257-10             5,624-10          7,750-01
           CAHCO3+           2,680-05             2,077-05          7,750-01
           CACO3             7,167-08             7,280-08          1,016+00
           CASO3             5,016-04             5,096-04          1,016+00
           CAHSO3+           5,253-04             4,071-04          7,750-01
           CASO4             9,784-04             9,940-04          1,016+00

           NA+               6,720-02             5,293-02          7,876-01
           NAOH              5,372-10             5,458-10          1,016+00
           NAHCO3            9,264-05             9,411-05          1,016+00
           NACO3-            4,348-07             3,370-07          7,750-01
           NASO3-            4,275-04             3,313-04          7,750-01
           NASO4-            2,697-03             2,090-03          7,750-01




           OH-               4,943-08             3,831-08          7,750-01
           CO3--             1,799-07             6,391-08          3,553-01
           SO3--             7,826-04             2,781-04          3,553-01
           SO4--             2,003-02             6,310-03          3,150-01

          COMPONENT          MOLALITY        ACTIVITY PRODUCT  RELATIVE SATURATION

           CA(OH)2(S)        0,000                7,460-19          2,569-13
           CACO3(S)          0,000                3,252-11          2,218-02
           CASO3(S)          0,000                1,414-07          2,193+00
           CASO4(S)          0,000                3,198-06          1,526-01

           PCO2 = 4,30463-01  ATM.
           PSO2 = 8,86985-09  ATM.

                      MOLECULAR WATER = 9,99683-01 KGS.

                    IONIC STRENGTH = 9,01060-02        RES. E.N. =   5,139-03
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RUN NO. 62

DATE 3/25/76

$e^{-T/\tau}$ 0.19

ANALYTICAL RESULTS

Species	Standards (mmoles/l)	Ca^+ Feed (mmole/l)	SO_3^{-2} Feed (mmole/l)	Effluent (mmole/l)	Solids (mmole/g)
Ca^{+2}		25		10.78	8.94
Mg^{+2}					
Na_2^{+1}			286	64.	
Cl^{-1}					
CO_3^{-2}		25			
Ts^{-2}			470	85.6	
SO_3^{-2}			182	36.4	5.24
SO_4^{-2}			288	52.8	.89

OPERATING DATA

Time (min)	pH	Temp. (°C)	SO_3^{-2} (mmole/l)	Solids Removal (ml/min)	Solids (wt%)	Solids (g)
60	5.69	55.3	31.5	25	0.44	14.2
120	5.69	54.8	32.8	55	.40	13.1

COMPUTER RESULTS

Ionic Strength	Residual Electroneutrality	Relative Saturation			Mole Fraction	
		$CaSO_3 \cdot \frac{1}{2}H_2O$	$CaSO_4 \cdot 2H_2O$	$CaSO_4 \cdot \frac{1}{2}H_2O$	SO_3^{-2}	SO_4^{-2}
0.160	0.020	7.46	0.49	0.24	0.83	0.17

REACTOR MATERIAL BALANCE CALCULATIONS

Run # 62 Date 3/25/76

INLET		A	B	Σ
Flow Rate (ml/min)		200	50.8	250.8
Ca^{+2}	(mmole/min)	4.94		4.94
Mg^{+2}	(mmole/min)			
Na_2^{+2}	(mmole/min)			
Cl^{-1}	(mmole/min)			
CO_3^{-2}	(mmole/min)	4.94		4.94
SO_3^{-2}	(mmole/min)		9.24	9.24
SO_4^{-2}	(mmole/min)		14.63	14.63

OUTLET		Liquid	Solid	Σ
Flow Rate (ml/min)		250.8	0.222 (g/min)	
Ca^{+2}	(mmole/min)	2.704	1.985	4.69
Mg^{+2}	(mmole/min)			
Na_2^{+2}	(mmole/min)			
Cl^{-1}	(mmole/min)			
Ts	(mmole/min)			
SO_3^{-2}	(mmole/min)	8.22	1.14	9.36
SO_4^{-2}	(mmole/min)	13.24	0.231	13.47

PREC. RATE	mmole/min	mmole/g	grams/min
Solid			0.222
Ca^{+2}	0.25	8.94	0.028
SO_3^{-2}	-0.12	5.12	0.023
SO_4^{-2}	1.16	1.04	1.11

SOLIDS MATERIAL BALANCE

Run No. 62

Date 3/25/76

	g/mmole	mmole/gram	g/gram
Ca^{++}	0.040	8.94	0.358
Mg^{++}	.024		
Na_2^{++}	.046		
Cl^-	.035		
$CO_3^=$	.060	(2.81)*	(.169)*
$SO_3^=$	.080	5.24	.419
$SO_4^=$	.096	.89	.085
$\frac{1}{2}H_2O$	.009	6.13	.055
			Σ 1.086

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* Excess calcium ([Ca] - [Ts]) is assumed to be calcium carbonate.

KINETIC RUN 62

```
14 APR 76    13:47:39,920                             TEMPERATURE    54,000 DEG. C.
                                  INPUT SPECIES (MOLES)

               H2O  = 5,55062+01                HCL  = 0,00000
               CAO  = 1,27800-02                CO2  = 2,22000-02
               MGO  = 0,00000                   N2O3 = 0,00000
               NA2O = 5,40000-02                N2O5 = 0,00000
                                                SO2  = 3,29000-02
                                                SO3  = 4,38000-02

          PH =  5,6900


          SUPERSATURATION ALLOWED

                         AQUEOUS SOLUTION EQUILIBRIA

          COMPONENT         MOLALITY          ACTIVITY     ACTIVITY COEFFICIENT

           H+               2,486-06          2,042-06          8,213-01
           H2O                                                  9,965-01
           H2CO3            1,445-02          1,486-02          1,028+00
           HCO3-            5,092-03          3,727-03          7,320-01
           H2SO3            5,434-05          5,589-05          1,028+00
           HSO3-            2,690-02          1,969-02          7,320-01
           HSO4-            5,429-06          4,036-06          7,434-01

           CA++             4,047-03          1,259-03          3,112-01
           CAOH+            1,696-09          1,260-09          7,434-01
           CAHCO3+          1,417-04          1,053-04          7,434-01
           CACO3            3,462-07          3,561-07          1,028+00
           CASO3            1,678-03          1,726-03          1,028+00
           CAHSO3+          1,844-03          1,371-03          7,434-01
           CASO4            3,075-03          3,163-03          1,028+00

           NA+              1,204-01          9,105-02          7,553-01
           NAOH             8,326-10          8,563-10          1,028+00
           NAHCO3           3,251-04          3,344-04          1,028+00
           NACO3-           1,548-06          1,151-06          7,434-01
           NASO3-           1,049-03          7,794-04          7,434-01
           NASO4-           6,298-03          4,682-03          7,434-01






           OH-              4,701-08          3,494-08          7,434-01
           CO3--            4,453-07          1,279-07          2,872-01
           SO3--            1,343-03          3,856-04          2,872-01
           SO4--            3,445-02          8,268-03          2,400-01

          COMPONENT         MOLALITY      ACTIVITY PRODUCT  RELATIVE SATURATION

           CA(OH)2(S)       0,000             1,537-18          3,145-13
           CACO3(S)         0,000             1,610-10          1,052-01
           CASO3(S)         0,000             4,847-07          7,459+00
           CASO4(S)         0,000             1,034-05          4,578-01

           PCO2 = 8,54793-01  ATM.
           PSO2 = 1,19933-05  ATM.

                         MOLECULAR WATER = 9,99431-01 KGS.

                       IONIC STRENGTH = 1,60537-01        RES. E.N. =  1,955-02
```

RUN NO. 63

DATE 3/29/76

$e^{-T/\tau}$ 0.37

ANALYTICAL RESULTS

Species	Standards (mmoles/1)	Ca^+ Feed (mmole/1)	SO_3^{-2} Feed (mmole/1)	Effluent (mmole/1)	Solids (mmole/g)
Ca^{+2}		25		14.9	
Mg^{+2}					
Na_2^{+1}			410	55.	
Cl^{-1}					
CO_3^{-2}		25			
Ts^{-2}			394	80.6	
SO_3^{-2}			110	19.4	2.04
SO_4^{-2}			300	61.2	.53

OPERATING DATA

Time (min)	pH	Temp. (°C)	SO_3^{-2} (mmole/1)	Solids Removal (ml/min)	Solids (wt%)	Solids (g)
33	5.71	55	17.99	25	0.0409	1.33
60	5.70	54.2	18.46	25	.050	1.62
130	5.68	55.	19.35	25	.050	1.62

COMPUTER RESULTS

Ionic Strength	Residual Electroneutrality	Relative Saturation			Mole Fraction	
		$CaSO_3 \cdot \frac{1}{2}H_2O$	$CaSO_4 \cdot 2H_2O$	$CaSO_4 \cdot \frac{1}{2}H_2O$	SO_3^{-2}	SO_4^{-2}
0.175	-0.0104	6.10	0.93	0.47	0.76	0.24

REACTOR MATERIAL BALANCE CALCULATIONS

Run # 63 Date 3/29/76

INLET		A	B	Σ
Flow Rate (ml/min)		200	50	250
Ca^{+2}	(mmole/min)	6.10		6.10
Mg^{+2}	(mmole/min)			
Na_2^{+2}	(mmole/min)		10.3	10.3
Cl^{-1}	(mmole/min)			
CO_3^{-2}	(mmole/min)	6.10		6.1
SO_3^{-2}	(mmole/min)		4.79	4.79
SO_4^{-2}	(mmole/min)		14.96	14.96

OUTLET		Liquid	Solid	Σ
Flow Rate (ml/min)		250	0.0125 (g/min)	
Ca^{+2}	(mmole/min)	3.73		3.73
Mg^{+2}	(mmole/min)			
Na_2^{+2}	(mmole/min)	13.75		13.8
Cl^{-1}	(mmole/min)			
CO_3^{-2}	(mmole/min)			
SO_3^{-2}	(mmole/min)	4.85	0.025	4.88
SO_4^{-2}	(mmole/min)	15.3	0.007	15.31

PREC. RATE	mmole/min	mmole/g	grams/min
Solid			
Ca^{+2}			
SO_3^{-2}			
SO_4^{-2}			

SOLIDS MATERIAL BALANCE

Run No. 63

Date 3/29/76

	g/mmole	mmole/gram	g/gram
Ca^{++}	0.040		
Mg^{++}	.024		
Na_2^{++}	.046		
Cl^-	.035		
$CO_3^=$	.060		
$SO_3^=$	.080	2.04	0.163
$SO_4^=$	.096	0.53	.051
$\frac{1}{2}H_2O$	.009	2.57	.023

Σ ______

KINETIC RUN 63

```
14 APR 78    15:47:40,053                              TEMPERATURE    55,000 DEG, C,
                                     INPUT SPECIES (MOLES)

                 H2O  = 5,55062+01               HCL  = 0,00000
                 CAO  = 1,49002-02               CO2  = 2,00000-02
                 MGO  = 0,00000                  N2O3 = 0,00000
                 NA2O = 5,50002-02               N2O5 = 0,00000
                                                 SO2  = 1,94000-02
                                                 SO3  = 6,12000-02

            PH =  5,7000

            SUPERSATURATION ALLOWED

                          AQUEOUS SOLUTION EQUILIBRIA

           COMPONENT           MOLALITY           ACTIVITY     ACTIVITY COEFFICIENT

            H+                 2,428-06           1,999-06          8,217-01
            H2O                                                     9,968-01
            H2CO3              1,431-02           1,475-02          1,031+00
            HCO3-              5,215-03           3,783-03          7,254-01
            H2SO3              2,993-06           3,086-06          1,031+00
            HSO3-              1,523-02           1,105-02          7,254-01
            HSO4-              7,212-06           5,328-06          7,388-01

            CA++               5,949-03           1,798-03          3,023-01
            CAOH+              2,557-09           1,889-09          7,388-01
            CAHCO3+            2,072-04           1,531-04          7,388-01
            CACO3              5,158-07           5,319-07          1,031+00
            CASO3              1,371-03           1,414-03          1,031+00
            CAHSO3+            1,500-03           1,108-03          7,388-01
            CASO4              5,800-03           6,063-03          1,031+00

            NA+                1,021-01           7,673-02          7,514-01
            NAOH               7,326-10           7,555-10          1,031+00
            NAHCO3             2,773-04           2,860-04          1,031+00
            NACO3-             1,371-06           1,013-06          7,388-01
            NASO3-             5,101-04           3,768-04          7,388-01
            NASO4-             7,139-03           5,273-03          7,388-01




            OH-                4,952-08           3,658-08          7,388-01
            CO3--              4,811-07           1,332-07          2,768-01
            SO3--              7,954-04           2,202-04          2,768-01
            SO4--              4,820-02           1,103-02          2,288-01
           COMPONENT           MOLALITY       ACTIVITY PRODUCT  RELATIVE SATURATION

            CA(OH)2(S)         0,000              2,407-18          8,129-13
            CACO3(S)           0,000              2,395-10          1,588-01
            CASO3(S)           0,000              3,954-07          6,101+00
            CASO4(S)           0,000              1,971-05          9,334-01

            PCO2 = 8,53785-01  ATM,
            PSO2 = 6,89906-08  ATM,

                         MOLECULAR WATER = 9,99540-01 KGS,

                       IONIC STRENGTH = 1,75883-01        RES, E,N, =  -1,037-02
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KINETIC RUN 63-B

```
03 MAY 76    16:12:34.394                                  TEMPERATURE    55.000 DEG. C.
                                   INPUT SPECIES (MOLES)

                   H2O  = 5.55062+01              HCL  = 0.00000
                   CAO  = 1.26000-02              CO2  = 0.00000
                   MGO  = 7.62000-01              N2O3 = 0.00000
                   NA2O = 2.74000-01              N2O5 = 0.00000
                                                  SO2  = 9.70000-02
                                                  SO3  = 1.00000+00

        PH =  5.7000

        SUPERSATURATION ALLOWED

                         AQUEOUS SOLUTION EQUILIBRIA

       COMPONENT          MOLALITY            ACTIVITY     ACTIVITY COEFFICIENT

        H+                1.231-06            1.995-06            1.621+00
        H2O                                                       9.692-01
        H2SO3             3.062-06            4.252-06            1.389+00
        HSO3-             2.660-02            1.522-02            5.723-01
        HSO4-             1.374-05            1.353-05            9.844-01

        CA++              4.013-03            1.101-03            2.743-01
        CAOH+             1.142-09            1.124-09            9.844-01
        CASO3             8.586-04            1.192-03            1.389+00
        CAHSO3+           9.491-04            9.342-04            9.844-01
        CASO4             6.786-03            9.424-03            1.389+00

        MG++              2.804-01            1.029-01            3.669-01
        MGOH+             2.061-06            2.029-06            9.844-01
        MGSO3             3.007-02            4.176-02            1.389+00
        MGHSO3+           3.326-02            3.274-02            9.844-01
        MGSO4             4.387-01            6.093-01            1.389+00

        NA+               4.816-01            3.623-01            7.524-01
        NAOH              2.498-09            3.469-09            1.389+00
        NASO3-            2.490-03            2.452-03            9.844-01
        NASO4-            6.423-02            6.323-02            9.844-01




        OH-               3.614-08            3.557-08            9.844-01
        SO3--             2.829-03            3.034-04            1.073-01
        SO4--             4.988-01            2.800-02            5.614-02

       COMPONENT          MOLALITY        ACTIVITY PRODUCT  RELATIVE SATURATION

        CA(OH)2(S)        0.000               1.393-16            4.704-13
        CASO3(S)          0.000               3.288-07            5.073+00
        CASO4(S)          0.000               2.896-05            1.372+00
        MG(OH)2(S)        0.000               1.302-16            1.456-05
        MGSO3(S)          0.000               2.842-05            6.498-01

        PSO2 = 9.49244-06  ATM.

                        MOLECULAR WATER = 9.99452-01 KGS.

                      IONIC STRENGTH = 1.87662+00        RES. E.N. =  -1.205-02
```

RUN NO. 64

DATE 4/02/76

$e^{-T/\tau}$ 0.131

ANALYTICAL RESULTS

Species	Standards (mmoles/1)	Ca^{+} Feed (mmole/1)	SO_3^{-2} Feed (mmole/1)	Effluent (mmole/1)	Solids (mmole/g)
Ca^{+2}		32.4		13.8	8.86
Mg^{+2}					
Na_2^{+1}		414	1400	710	
Cl^{-1}		828	700	784	
CO_3^{-2}		32.4		5.2	(6.97)
Ts^{-2}			567	329	
SO_3^{-2}			108	38.7	1.79
SO_4^{-2}			459	290.	0.10

OPERATING DATA

Time min)	pH	Temp. (°C)	SO_3^{-2} (mmole/1)	Solids Removal (ml/min)	Solids (wt%)	Solids (g)
25	5.84	54.1	37.1	25	0.365	11.9
180	5.90	53.2	38.0	30	.296	9.62
220	5.93	53.	38.7			

COMPUTER RESULTS

Ionic Strength	Residual Electroneutrality	Relative Saturation $CaSO_3 \cdot \frac{1}{2}H_2O$	Relative Saturation $CaSO_4 \cdot 2H_2O$	Relative Saturation $CaSO_4 \cdot \frac{1}{2}H_2O$	Mole Fraction SO_3^{-2}	Mole Fraction SO_4^{-2}
1.523	0.025	10.1	0.848	0.41	0.91	0.09

REACTOR MATERIAL BALANCE CALCULATIONS

Run # 64 Date 4/02/76

INLET		A	B	Σ
Flow Rate (ml/min)		192.3	101	293.3
Ca^{+2}	(mmole/min)	6.23		6.23
Mg^{+2}	(mmole/min)			
Na_2^{+2}	(mmole/min)	79.6	142	222.
Cl^{-1}	(mmole/min)	159.	70.7	230.
CO_3^{-2}	(mmole/min)	6.23		6.23
SO_3^{-2}	(mmole/min)		10.91	10.91
SO_4^{-2}	(mmole/min)		46.36	46.36

OUTLET		Liquid	Solid	Σ
Flow Rate (ml/min)		293.3	0.089 (g/min)	
Ca^{+2}	(mmole/min)	4.05	0.788	4.84
Mg^{+2}	(mmole/min)			
Na_2^{+2}	(mmole/min)	208.2		208.
Cl^{-1}	(mmole/min)	230.		230.
CO_3^{-2}	(mmole/min)	1.53	0.677	2.21
SO_3^{-2}	(mmole/min)	11.35	0.10	11.45
SO_4^{-2}	(mmole/min)	84.76	0.01	85.77

PREC. RATE	mmole/min	mmole/g	grams/min
Solid			0.089
Ca^{+2}	1.39	8.86	0.157
SO_3^{-2}	0.54	1.13	0.478
SO_4^{-2}	-38.4	.116	-331.0

SOLIDS MATERIAL BALANCE

Run No. 64

Date 4/02/76

	g/mmole	mmole/gram	g/gram
Ca^{++}	0.040	8.86	0.354
Mg^{++}	.024		
Na_2^{++}	.046		
Cl^-	.035		
$CO_3^=$	.060	(6.97)*	(.418)*
$SO_3^=$	.080	1.79	.143
$SO_4^=$	.096	.10	.010
$\frac{1}{2}H_2O$	.009	1.89	.017
		Σ	.942

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* Excess calcium ([Ca] - [Ts]) is assumed to be calcium carbonate.

KINETIC RUN 64

```
03 MAY 76    10112100,035
                                                      TEMPERATURE    53.000 DEG. C.
                       INPUT SPECIES (MOLES)

            H2O  = 5,55262+01                  HCL  = 7,84200-01
            CAO  = 1,38203-02                  CO2  = 5,20000-03
            MGO  = 0,00000                     N2O3 = 0,00000
            NA2O = 7,12000-01                  N2O5 = 0,00000
                                               SO2  = 3,87000-02
                                               SO3  = 2,09300-01

      PH =  5,0329

      SUPERSATURATION ALLOWED

                   AQUEOUS SOLUTION EQUILIBRIA

      COMPONENT         MOLALITY          ACTIVITY       ACTIVITY COEFFICIENT

       H+               8,553-07          1,175-06            1,374+00
       H2O                                                    9,803-01
       H2CO3            2,137-03          2,789-03            1,305+00
       HCO3-            2,087-03          1,220-03            5,845-01
       H2SO3            1,524-06          1,902-06            1,305+00
       HSO3-            2,145-02          1,254-02            5,845-01
       HSO4-            3,836-06          3,414-06            8,899-01

       CA++             6,202-03          1,546-03            2,493-01
       CAOH+            2,633-09          2,343-09            8,899-01
       CAHCO3+          4,707-05          4,188-05            8,899-01
       CACO3            1,851-07          2,416-07            1,305+00
       CASO3            1,895-03          2,356-03            1,305+00
       CAHSO3+          1,163-03          1,035-03            8,899-01
       CASO4            4,489-03          5,860-03            1,305+00

       NA+              1,314+00          9,626-01            7,326-01
       NAOH             1,060-06          1,384-06            1,305+00
       NAHCO3           8,861-04          1,157-03            1,305+00
       NACO3-           7,608-06          6,763-06            8,899-01
       NASO3-           1,028-02          9,146-03            8,899-01
       NASO4-           8,530-02          7,591-02            8,899-01




       OH-              6,002-08          5,341-08            8,899-01
       CL-              7,787-01          4,365-01            5,606-01
       CO3--            6,153-07          7,182-08            1,167-01
       SO3--            3,737-03          4,362-04            1,167-01
       SO4--            1,585-01          1,279-02            6,448-02
     COMPONENT          MOLALITY      ACTIVITY PRODUCT   RELATIVE SATURATION

       CA(OH)2(S)       0,000             4,412-18            1,423-12
       CACO3(S)         0,000             1,110-10            6,854-02
       CASO3(S)         0,000             5,609-07            1,006+01
       CASO4(S)         0,000             1,823-05            6,480-01
      PCO2 = 1,55387-01  ATM,
      PSO2 = 4,22614-06  ATM,

                  MOLECULAR WATER = 1,00679+00 KGS,

               IONIC STRENGTH = 1,52342+00        RES, E.N, =   2,509-02
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RUN NO. 65

DATE 4/05/75

$e^{-T/\tau}$ 0.03

ANALYTICAL RESULTS

Species	Standards (mmoles/1)	Ca^+ Feed (mmole/1)	SO_3^{-2} Feed (mmole/1)	Effluent (mmole/1)	Solids (mmole/g)
Ca^{+2}		30		7.75	9.88
Mg^{+2}			1130	574.	
Na^{+1}			500	155.	
Cl^{-1}					
CO_3^{-2}		30		4.7	
Ts^{-2}			160	855.	
SO_3^{-2}			500	155.	1.17
SO_4^{-2}			1750	700.	0.05

OPERATING DATA

Time (min)	pH	Temp. (°C)	SO_3^{-2} (mmole/1)	Solids Removal (ml/min)	Solids (wt%)	Solids (g)
46	5.8	55		50	0.56	18.2
100	5.8	55		80	.51	16.5
160	5.8	55	155	80		

COMPUTER RESULTS

Ionic Strength	Residual Electroneutrality	Relative Saturation			Mole Fraction	
		$CaSO_3 \cdot \frac{1}{2}H_2O$	$CaSO_4 \cdot 2H_2O$	$CaSO_4 \cdot \frac{1}{2}H_2O$	SO_3^{-2}	SO_4^{-2}
1.40	-0.144	6.03	0.64	0.32	0.95	0.05

REACTOR MATERIAL BALANCE CALCULATIONS

Run # 65 Date 4/05/76

INLET		A	B	Σ
Flow Rate (ml/min)		200	100	300
Ca^{+2}	(mmole/min)	5.98	---	5.98
Mg^{+2}	(mmole/min)		167	167.
Na_2^{+2}	(mmole/min)		35.8	35.8
Cl^{-1}	(mmole/min)			
CO_3^{-2}	(mmole/min)	5.98		5.98
SO_3^{-2}	(mmole/min)		50.0	50.0
SO_4^{-2}	(mmole/min)		174.0	174.

OUTLET		Liquid	Solid	Σ
Flow Rate (ml/min)		300	0.406 (g/min)	
Ca^{+2}	(mmole/min)	2.32	4.01	6.33
Mg^{+2}	(mmole/min)	172		172.
Na_2^{+2}	(mmole/min)	46.5		46.5
Cl^{-1}	(mmole/min)			
CO_3^{-2}	(mmole/min)	1.41	3.52	4.93
SO_3^{-2}	(mmole/min)	46.5	0.48	47.0
SO_4^{-2}	(mmole/min)	210.	0.02	210.

PREC. RATE	mmole/min	mmole/g	grams/min
Solid			0.406
Ca^{+2}	6.64	9.88	.672
SO_3^{-2}	3.5	1.17	3.0
SO_4^{-2}	-36.	0.05	- 0.720

SOLIDS MATERIAL BALANCE

Run No. 65

Date 4/05/76

	g/mmole	mmole/gram	g/gram
Ca^{++}	0.040	9.88	0.395
Mg^{++}	.024		
Na_2^{++}	.046		
Cl^-	.035		
$CO_3^=$	.060	(8.66)*	(.520)*
$SO_3^=$	.080	1.17	.094
$SO_4^=$	.096	.050	.005
$\frac{1}{2}H_2O$	.009	1.22	.011
		Σ	1.025

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* Excess calcium ([Ca] - [Ts]) is assumed to be calcium carbonate.

KINETIC RUN 65

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03 MAY 79    18:12:07,525                                   TEMPERATURE    55,000 DEG. C.
                                 INPUT SPECIES (MOLES)

                  H2O  = 5,55062+01            HCL  = 0,00000
                  CAO  = 7,75200-03            CO2  = 4,72300-03
                  MGO  = 5,74000-01            N2O3 = 0,00000
                  NA2O = 1,55200-01            N2O5 = 0,00000
                                               SO2  = 1,55000-01
                                               SO3  = 7,00000-01

            PH =  5,800

            SUPERSATURATION ALLOWED

                          AQUEOUS SOLUTION EQUILIBRIA

           COMPONENT         MOLALITY         ACTIVITY     ACTIVITY COEFFICIENT

            H+               1,218-05         1,585-06          1,301+00
            H2O                                                 9,792-01
            H2CO3            2,235-03         2,857-03          1,278+00
            HCO3-            1,588-03         9,223-04          5,881-01
            H2SO3            5,027-06         6,423-06          1,278+00
            HSO3-            4,922-02         2,895-02          5,881-01
            HSO4-            1,153-05         9,930-06          8,610-01

            CA++             2,256-03         5,437-04          2,410-01
            CAOH+            8,284-10         7,063-10          8,610-01
            CAHCO3+          1,310-05         1,128-05          8,610-01
            CACO3            3,863-08         4,935-08          1,278+00
            CASO3            1,103-03         1,410-03          1,278+00
            CAHSO3+          1,019-03         8,775-04          8,610-01
            CASO4            3,366-03         4,301-03          1,278+00

            MG++             2,046-01         6,426-02          3,141-01
            MGOH+            1,872-06         1,612-06          8,610-01
            MGHCO3+          7,385-04         6,359-04          8,610-01
            MGCO3            7,340-06         9,379-06          1,278+00
            MGSO3            4,887-02         6,245-02          1,278+00
            MGHSO3+          4,516-02         3,888-02          8,610-01
            MGSO4            2,752-01         3,516-01          1,278+00



            NA+              2,698-01         1,958-01          7,259-01
            NAOH             1,866-09         2,385-09          1,278+00
            NAHCO3           1,393-04         1,779-04          1,278+00
            NACO3-           9,215-07         7,934-07          8,610-01
            NASO3-           3,684-03         3,172-03          8,610-01
            NASO4-           3,667-02         3,157-02          8,610-01

            OH-              5,255-08         4,525-08          8,610-01
            CO3--            3,418-07         4,088-08          1,196-01
            SO3--            6,073-03         7,263-04          1,196-01
            SO4--            3,854-01         2,587-02          6,714-02

           COMPONENT         MOLALITY      ACTIVITY PRODUCT  RELATIVE SATURATION

            CA(OH)2(S)       0,000            1,113-18          3,759-13
            CACO3(S)         0,000            2,223-11          1,473-02
            CASO3(S)         0,000            3,909-07          6,030+00
            CASO4(S)         0,000            1,349-05          8,389-01
            MG(OH)2(S)       0,000            1,315-16          1,472-05
            MGCO3(S)         0,000            2,467-09          2,252-04
            MGSO3(S)         0,000            4,383-05          1,081+00

            PCO2 = 1,74616-01  ATM.
            PSO2 = 1,41919-05  ATM.

                       MOLECULAR WATER = 9,99879-01 KGS.

                    IONIC STRENGTH = 1,40492+00       RES. E.N. =  -1,430-01
```

RUN NO. 66

DATE 4/05/76

$e^{-T/\tau}$ 0.08

ANALYTICAL RESULTS

Species	Standards (mmoles/l)	Ca^{+} Feed (mmole/l)	SO_3^{-2} Feed (mmole/l)	Effluent (mmole/l)	Solids (mmole/g)
Ca^{+2}		30		7.00	8.94
Mg^{+2}			1130	516.	
Na_2^{+1}			500	156.	
Cl^{-1}					
CO_3^{-2}		30		3.5	
Ts^{-2}			160	795.	
SO_3^{-2}			500	148.	0.95
SO_4^{-2}			1310	647	0.05

OPERATING DATA

Time (min)	pH	Temp. (°C)	SO_3^{-2} (mmole/l)	Solids Removal (ml/min)	Solids (wt%)	Solids (g)
45	5.89	59.1		105	0.482	13.3
70	5.89	58.	148	105	.447	12.3

COMPUTER RESULTS

Ionic Strength	Residual Electroneutrality	Relative Saturation			Mole Fraction	
		$CaSO_3 \cdot \frac{1}{2}H_2O$	$CaSO_4 \cdot 2H_2O$	$CaSO_4 \cdot \frac{1}{2}H_2O$	SO_3^{-2}	SO_4^{-2}
1.317	-0.148	5.85	0.55	0.29	0.95	0.05

REACTOR MATERIAL BALANCE CALCULATIONS

Run # 66 Date 4/05/76

INLET		A	B	Σ
Flow Rate (ml/min)		200	100	300
Ca^{+2}	(mmole/min)	5.98		5.98
Mg^{+2}	(mmole/min)		128	128.
Na_2^{+2}	(mmole/min)		32.3	32.3
Cl^{-1}	(mmole/min)			
CO_3^{-2}	(mmole/min)	5.98		5.98
SO_3^{-2}	(mmole/min)		40.0	40.0
SO_4^{-2}	(mmole/min)		120.0	120.0

OUTLET		Liquid	Solid	Σ
Flow Rate (ml/min)		300	0.397 (g/min)	
Ca^{+2}	(mmole/min)	2.10	3.55	5.65
Mg^{+2}	(mmole/min)	155.		155.
Na_2^{+2}	(mmole/min)	46.8		46.8
Cl^{-1}	(mmole/min)			
CO_3^{-2}	(mmole/min)	1.05	3.15	4.20
SO_3^{-2}	(mmole/min)	44.4	0.38	445.
SO_4^{-2}	(mmole/min)	194.	0.02	194.

PREC. RATE	mmole/min	mmole/g	grams/min
Solid			0.397
Ca^{+2}	3.88	8.94	0.434
SO_3^{-2}	-4.4	0.95	-4.63
SO_4^{-2}	-74.	0.05	-1480.

SOLIDS MATERIAL BALANCE

Run No. 66

Date 4/05/76

	g/mmole	mmole/gram	g/gram
Ca^{++}	0.040	8.94	0.358
Mg^{++}	.024		
Na_2^{++}	.046		
Cl^-	.035		
$CO_3^=$	.060	(7.94)*	(0.476)*
$SO_3^=$	.080	0.95	.076
$SO_4^=$	.096	0.05	.005
$\frac{1}{2}H_2O$	.009	1.00	.009
			Σ 0.924

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* Excess calcium ([Ca] - [Ts]) is assumed to be calcium carbonate.

KINETIC RUN 66

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03 MAY 76    10112109,198                                       TEMPERATURE    50,000 DEG. C.
                                  INPUT SPECIES (MOLES)

                  H2O  = 5,55082+01            HCL  = 0,00000
                  CAO  = 7,00000-03            CO2  = 3,50000-03
                  MGO  = 5,10000-01            N2O3 = 0,00000
                  NA2O = 1,56000-01            N2O5 = 0,00000
                                               SO2  = 1,48400-01
                                               SO3  = 6,47000-01

        PH =  5,8902


        SUPERSATURATION ALLOWED

                       AQUEOUS SOLUTION EQUILIBRIA

       COMPONENT          MOLALITY             ACTIVITY      ACTIVITY COEFFICIENT

        H+                1,025-06             1,288-06             1,256+00
        H2O                                                         9,807-01
        H2CO3             1,531-03             1,929-03             1,259+00
        HCO3-             1,285-03             7,581-04             5,899-01
        H2SO3             4,071-06             5,128-06             1,259+00
        HSO3-             4,568-02             2,695-02             5,899-01
        HSO4-             1,024-05             8,626-06             8,423-01

        CA++              1,998-03             4,699-04             2,351-01
        CAOH+             1,073-09             9,039-10             8,423-01
        CAHCO3+           9,700-06             8,170-06             8,423-01
        CACO3             3,602-08             4,537-08             1,259+00
        CASO3             1,099-03             1,384-03             1,259+00
        CAHSO3+           8,936-04             7,526-04             8,423-01
        CASO4             3,005-03             3,784-03             1,259+00

        MG++              1,846-01             5,634-02             3,053-01
        MGOH+             2,523-06             2,125-06             8,423-01
        MGHCO3+           5,524-04             4,652-04             8,423-01
        MGCO3             6,957-06             8,762-06             1,259+00
        MGSO3             5,047-02             6,356-02             1,259+00
        MGHSO3+           3,910-02             3,293-02             8,423-01
        MGSO4             2,417-01             3,045-01             1,259+00




        NA+               2,710-01             1,954-01             7,210-01
        NAOH              2,749-09             3,462-09             1,259+00
        NAHCO3            1,159-04             1,459-04             1,259+00
        NACO3-            9,886-07             8,327-07             8,423-01
        NASO3-            4,280-03             3,605-03             8,423-01
        NASO4-            3,688-02             3,107-02             8,423-01

        OH-               7,817-08             6,584-08             8,423-01
        CO3--             3,485-07             4,218-08             1,211-01
        SO3--             6,600-03             7,992-04             1,211-01
        SO4--             3,659-01             2,513-02             6,868-02

       COMPONENT          MOLALITY        ACTIVITY PRODUCT  RELATIVE SATURATION

        CA(OH)2(S)        0,000                2,037-18             7,375-13
        CACO3(S)          0,000                1,082-11             1,460-02
        CASO3(S)          0,000                3,718-07             5,855+00
        CASO4(S)          0,000                1,136-05             5,539-01
        MG(OH)2(S)        0,000                2,442-16             2,017-05
        MGCO3(S)          0,000                2,242-09             2,174-04
        MGSO3(S)          0,000                4,246-05             1,053+00

        PCO2 = 1,25517-01  ATM,
        PSO2 = 1,23423-05  ATM,

                   MOLECULAR WATER = 9,99183-01 KGS.

                 IONIC STRENGTH = 1,31793+00        RES. E.N. =  -1,485-01
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RUN NO. 67

DATE 4/06/76

$e^{-T/\tau}$ 0.35

ANALYTICAL RESULTS

Species	Standards (mmoles/1)	Ca^{+} Feed (mmole/1)	SO_3^{-2} Feed (mmole/1)	Effluent (mmole/1)	Solids (mmole/g)
Ca^{+2}		30		6.98	9.43
Mg^{+2}			1300	436	
Na^{+1}			500	166	
Cl^{-1}					
CO_3^{-2}		30		5.4	
Ts^{-2}			1580	686.	
SO_3^{-2}			500	159.	0.474
SO_4^{-2}			1540	527	0.035

OPERATING DATA

Time (min)	pH	Temp. (°C)	SO_3^{-2} (mmole/1)	Solids Removal (ml/min)	Solids (wt%)	Solids (g)
30	5.81	42.4		84	0.404	13.2
50	5.80	41.2		115		
60	5.80	41.2		115	.326	10.6
100	5.79	43.	159	122	.267	8.6

COMPUTER RESULTS

Ionic Strength	Residual Electroneutrality	Relative Saturation			Mole Fraction	
		$CaSO_3 \cdot \frac{1}{2}H_2O$	$CaSO_4 \cdot 2H_2O$	$CaSO_4 \cdot \frac{1}{2}H_2O$	SO_3^{-2}	SO_4^{-2}
1.16	-0.057	7.46	0.50	0.19	0.98	0.03

REACTOR MATERIAL BALANCE CALCULATIONS

Run # 67 Date 4/06/76

INLET		A	B	Σ
Flow Rate (ml/min)		182.9	105.3	288.2
Ca^{+2}	(mmole/min)	6.05		6.05
Mg^{+2}	(mmole/min)		124.	124.
Na_2^{+2}	(mmole/min)		39.9	39.9
Cl^{-1}	(mmole/min)			
CO_3^{-2}	(mmole/min)	6.05		6.05
SO_3^{-2}	(mmole/min)		52.7	52.7
SO_4^{-2}	(mmole/min)		162.2	162.2

OUTLET		Liquid	Solid		Σ
Flow Rate (ml/min)		288.2	0.324	(g/min)	
Ca^{+2}	(mmole/min)	2.01	3.06		5.07
Mg^{+2}	(mmole/min)	126.			126.
Na_2^{+2}	(mmole/min)	47.7			47.7
Cl^{-1}	(mmole/min)				
CO_3^{-2}	(mmole/min)	1.55			
SO_3^{-2}	(mmole/min)	45.8	0.15		46.0
SO_4^{-2}	(mmole/min)	151.9	0.003		151.9

PREC. RATE	mmole/min	mmole/g	grams/min
Solid			0.324
Ca^{+2}	4.04	9.43	0.428
SO_3^{-2}	6.8	0.474	14.4
SO_4^{-2}	10.3	0.35	294.

SOLIDS MATERIAL BALANCE

Run No. 67

Date 4/06/76

	g/mmole	mmole/gram	g/gram
Ca^{++}	0.040	9.43	0.397
Mg^{++}	.024		
Na_2^{++}	.046		
Cl^-	.035		
$CO_3^=$	.060	(8.92)	(.597)*
$SO_3^=$	.080	0.474	.038
$SO_4^=$	.096	.035	.003
$\frac{1}{2}H_2O$	.009	.509	.005
		Σ	1.040

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* Excess calcium ([Ca] - [Ts]) is assumed to be calcium carbonate.

KINETIC RUN 67

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19 APR 78    10100138,293                                  TEMPERATURE    43,000 DEG. C.
                                 INPUT SPECIES (MOLES)

                H2O  = 5,55062+01                HCL  = 0,00000
                CAO  = 8,90000-03                CO2  = 5,40000-03
                MGO  = 4,36000-01                N2O3 = 0,00000
                NA2O = 1,66000-01                N2O5 = 0,00000
                                                 SO2  = 1,59000-01
                                                 SO3  = 5,27000-01

        PH =  5,7900

        SUPERSATURATION ALLOWED

                   AQUEOUS SOLUTION EQUILIBRIA

       COMPONENT          MOLALITY          ACTIVITY     ACTIVITY COEFFICIENT

        H+                1,395-06          1,622-06           1,163+00
        H2O                                                    9,823-01
        H2CO3             2,777-03          3,405-03           1,226+00
        HCO3-             1,774-03          1,073-03           6,049-01
        H2SO3             5,348-06          6,557-06           1,226+00
        HSO3-             5,976-02          3,615-02           6,049-01
        HSO4-             7,912-06          6,430-06           8,128-01

        CA++              2,141-03          5,057-04           2,362-01
        CAOH+             3,589-10          2,917-10           8,128-01
        CAHCO3+           1,386-05          1,127-05           8,128-01
        CACO3             3,341-06          4,096-06           1,226+00
        CASO3             1,351-03          1,657-03           1,226+00
        CAHSO3+           9,593-04          7,797-04           8,128-01
        CASO4             2,521-03          3,091-03           1,226+00

        MG++              1,631-01          4,912-02           3,011-01
        MGOH+             6,305-07          5,125-07           8,128-01
        MGHCO3+           6,535-04          5,312-04           8,128-01
        MGCO3             5,177-06          6,347-06           1,226+00
        MGSO3             4,489-02          5,504-02           1,226+00
        MGHSO3+           3,913-02          3,180-02           8,128-01
        MGSO4             1,886-01          2,312-01           1,226+00




        NA+               2,910-01          2,095-01           7,200-01
        NAOH              9,936-10          1,218-09           1,226+00
        NAHCO3            1,806-04          2,214-04           1,226+00
        NACO3-            9,755-07          7,928-07           8,128-01
        NASO3-            5,211-03          4,235-03           8,128-01
        NASO4-            3,596-02          2,923-02           8,128-01

        OH-               2,658-08          2,160-08           8,128-01
        CO3--             3,093-07          4,142-08           1,339-01
        SO3--             7,847-03          1,049-03           1,339-01
        SO4--             3,004-01          2,387-02           7,946-02

       COMPONENT          MOLALITY        ACTIVITY PRODUCT  RELATIVE SATURATION

        CA(OH)2(S)        0,000             2,360-19           6,090-14
        CACO3(S)          0,000             2,094-11           8,921-03
        CASO3(S)          0,000             5,260-07           7,456+00
        CASO4(S)          0,000             1,165-05           5,045-01
        MG(OH)2(S)        0,000             2,202-17           2,256-06
        MGCO3(S)          0,000             1,927-09           1,364-04
        MGSO3(S)          0,000             4,888-05           7,729-01

        PCO2 = 1,50275-01  ATM.
        PSO2 = 1,00272-05  ATM.

                   MOLECULAR WATER = 9,99028-01 KGS.

                 IONIC STRENGTH = 1,16431+00        RES. E.N. =  -5,897-02
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RUN NO. 68 $e^{-T/\tau}$ 0.063

DATE 4/08/76

ANALYTICAL RESULTS

Species	Standards (mmoles/1)	Ca^{+} Feed (mmole/1)	SO_3^{-2} Feed (mmole/1)	Effluent (mmole/1)	Solids (mmole/g)
a^{+2}		18		7.79	8.52
Mg^{+2}			1200	404.	
a_2^{+1}			315	148.	
Cl^{-1}					
O_3^{-2}		18		4.7	0.852
Ts^{-2}			1490	540.	
O_3^{-2}			315	92.	.852
SO_4^{-2}			1350	448	.035

OPERATING DATA

Time in)	pH	Temp. (°C)	SO_3^{-2} (mmole/1)	Solids Removal (ml/min)	Solids (wt%)	Solids (g)
60	5.72	53.0		30	0.28	9.1
120	5.72	52.4		30	.28	9.1
180	5.70	51.2		30	.21	6.6
240	5.69	50.2		30	.142	4.5
300	5.67	51.3	92.1	30	.146	4.6

COMPUTER RESULTS

Ionic Strength	Residual Electroneutrality	Relative Saturation			Mole Fraction	
		$CaSO_3 \cdot \frac{1}{2}H_2O$	$CaSO_4 \cdot 2H_2O$	$CaSO_4 \cdot \frac{1}{2}H_2O$	SO_3^{-2}	SO_4^{-2}
1.03	0.101	4.12	0.58	0.27	0.96	0.04

REACTOR MATERIAL BALANCE CALCULATIONS

Run # 68 Date 4/08/76

INLET		A	B	Σ
Flow Rate (ml/min)		201.3	99.2	300.5
Ca^{+2}	(mmole/min)	3.60	----	3.60
Mg^{+2}	(mmole/min)		113.	113.
Na_2^{+2}	(mmole/min)			
Cl^{-1}	(mmole/min)			
CO_3^{-2}	(mmole/min)	3.60		3.6
SO_3^{-2}	(mmole/min)		31.3	31.3
SO_4^{-2}	(mmole/min)		134.	134.

OUTLET		Liquid	Solid	Σ
Flow Rate (ml/min)		300.5	0.042 (g/min)	
Ca^{+2}	(mmole/min)	2.34	0.36	2.70
Mg^{+2}	(mmole/min)	121.		121.
Na_2^{+2}	(mmole/min)	44.5		44.5
Cl^{-1}	(mmole/min)			
CO_3^{-2}	(mmole/min)	1.41		
SO_3^{-2}	(mmole/min)	27.6	0.04	27.7
SO_4^{-2}	(mmole/min)	1.35	0.01	135.

PREC. RATE	mmole/min	mmole/g	grams/min
Solid			0.042
Ca^{+2}	1.26	8.52	0.148
SO_3^{-2}	3.61	0.852	4.24
SO_4^{-2}	-0.7	0.064	-10.9

SOLIDS MATERIAL BALANCE

Run No. 68

Date 4/08/76

	g/mmole	mmole/gram	g/gram
Ca^{++}	0.040	8.52	0.341
Mg^{++}	.024		
Na_2^{++}	.046		
Cl^-	.035		
$CO_3^=$	.060	(7.60)*	(.456)*
$SO_3^=$	.080	0.852	.068
$SO_4^=$	.096	.064	.006
$\frac{1}{2}H_2O$	.009	.916	.008
		Σ	0.879

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* Excess calcium ([Ca] - [Ts]) is assumed to be calcium carbonate.

KINETIC RUN 68

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19 APR 76    10108140,019                                      TEMPERATURE    51,300 DEG, C,
                                  INPUT SPECIES (MOLES)

                  H2O  = 5,55062+01                    HCL  = 0,00000
                  CAO  = 7,79000-03                    CO2  = 4,72000-03
                  MGO  = 4,24000-01                    N2O3 = 0,00000
                  NA2O = 1,48000-01                    N2O5 = 0,00000
                                                       SO2  = 9,27000-02
                                                       SO3  = 4,48000-01

        PH =  5,6700


        SUPERSATURATION ALLOWED

                     AQUEOUS SOLUTION EQUILIBRIA

        COMPONENT          MOLALITY           ACTIVITY     ACTIVITY COEFFICIENT

         H+                1,942-06           2,138-06          1,101+00
         H2O                                                    9,847-01
         H2CO3             2,726-03           3,263-03          1,197+00
         HCO3-             1,294-03           7,866-04          6,079-01
         H2SO3             4,985-06           5,968-06          1,197+00
         HSO3-             3,509-02           2,133-02          6,079-01
         HSO4-             1,162-05           9,139-06          7,863-01

         CA++              2,904-03           6,608-04          2,276-01
         CAOH+             6,439-10           5,063-10          7,863-01
         CAHCO3+           1,452-05           1,142-05          7,863-01
         CACO3             2,962-08           3,546-08          1,197+00
         CASO3             7,901-04           9,459-04          1,197+00
         CAHSO3+           9,222-04           7,252-04          7,863-01
         CASO4             3,165-03           3,789-03          1,197+00

         MG++              1,778-01           5,122-02          2,881-01
         MGOH+             9,450-07           7,431-07          7,863-01
         MGHCO3+           5,397-04           4,244-04          7,863-01
         MGCO3             3,682-06           4,409-06          1,197+00
         MGSO3             2,233-02           2,673-02          1,197+00
         MGHSO3+           2,773-02           2,181-02          7,863-01
         MGSO4             1,759-01           2,105-01          1,197+00




         NA+               2,648-01           1,887-01          7,127-01
         NAOH              1,157-09           1,385-09          1,197+00
         NAHCO3            1,222-04           1,463-04          1,197+00
         NACO3-            5,827-07           4,582-07          7,863-01
         NASO3-            2,138-03           1,681-03          7,863-01
         NASO4-            2,912-02           2,290-02          7,863-01

         OH-               3,469-08           2,727-08          7,863-01
         CO3--             1,838-07           2,510-08          1,366-01
         SO3--             3,056-03           4,174-04          1,366-01
         SO4--             2,401-01           1,985-02          8,265-02

        COMPONENT          MOLALITY       ACTIVITY PRODUCT  RELATIVE SATURATION

         CA(OH)2(S)        0,000              4,916-19          1,526-13
         CACO3(S)          0,000              1,559-11          9,629-03
         CASO3(S)          0,000              2,737-07          4,117+00
         CASO4(S)          0,000              1,272-05          5,832-01
         MG(OH)2(S)        0,000              3,810-17          4,102-06
         MGCO3(S)          0,000              1,228-09          1,038-04
         MGSO3(S)          0,000              2,042-05          4,190-01

         PCO2 = 1,82980-01  ATM,
         PSO2 = 1,17522-05  ATM,

                     MOLECULAR WATER = 9,99359-01 KGS,

                IONIC STRENGTH = 1,02881+00       RES, E,N, =   1,014-01
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RUN NO. 69

DATE 4/27/76

$e^{-T/\tau}$ > 0.01

ANALYTICAL RESULTS

Species	Standards (mmoles/l)	Ca^{+} Feed (mmole/l)	SO_3^{-2} Feed (mmole/l)	Effluent (mmole/l)	Solids (mmole/g)
Ca^{+2}		40.0		9.3	7.68
Mg^{+2}					
Na_2^{+1}			26.6	13.0	
Cl^{-1}		77.7	0.	38.4	
CO_3^{-2}					7.47
Ts^{-2}			27.2	2.76	
SO_3^{-2}			21.2	.70	7.02
SO_4^{-2}			6.0	2.06	0.478

OPERATING DATA

Time (min)	pH	Temp. (°C)	SO_3^{-2} (mmole/l)	Solids Removal (ml/min)	Solids (wt%)	Solids (g)
90	7.91	50.2	0.70	125	0.194	6.29

COMPUTER RESULTS

Ionic Strength	Residual Electroneutrality	Relative Saturation			Mole Fraction	
		$CaSO_3\cdot\frac{1}{2}H_2O$	$CaSO_4\cdot 2H_2O$	$CaSO_4\cdot\frac{1}{2}H_2O$	SO_3^{-2}	SO_4^{-2}
0.051	0.0007	2.45	0.092	0.042	0.936	0.064

REACTOR MATERIAL BALANCE CALCULATIONS

Run # 69 Date 4/27/76

INLET		A	B	Σ
Flow Rate (ml/min)		100	100	200
Ca^{+2}	(mmole/min)	4.0		4.0
Mg^{+2}	(mmole/min)			
Na_2^{+2}	(mmole/min)		2.66	2.66
Cl^{-1}	(mmole/min)	7.77		7.77
Ts	(mmole/min)			
SO_3^{-2}	(mmole/min)		2.12	2.12
SO_4^{-2}	(mmole/min)		.60	0.60

OUTLET		Liquid	Solid		Σ
Flow Rate (ml/min)		200	0.243	(g/min)	
Ca^{+2}	(mmole/min)	1.86	1.86		3.72
Mg^{+2}	(mmole/min)				
Na_2^{+2}	(mmole/min)	2.60			2.60
Cl^{-1}	(mmole/min)	7.68			7.68
Ts	(mmole/min)				
SO_3^{-2}	(mmole/min)	0.14	1.70		1.84
SO_4^{-2}	(mmole/min)	0.412	0.116		0.53

PREC. RATE	mmole/min	mmole/g	grams/min
Solid			0.243
Ca^{+2}	2.14	7.68	0.229
SO_3^{-2}	1.98	7.02	0.282
SO_4^{-2}	0.188	0.478	0.39

SOLIDS MATERIAL BALANCE

Run No. 69

Date 4/27/76

	g/mmole	mmole/gram	g/gram
Ca^{++}	0.040	7.68	0.307
Mg^{++}	.024		
Na_2^{++}	.046		
Cl^-	.035		
$CO_3^=$	.060		
$SO_3^=$	.080	7.02	.562
$SO_4^=$	.096	.48	.046
$\frac{1}{2}H_2O$	.009	7.50	.067

Σ 0.982

KINETIC RUN 69

```
03 MAY 76    10:12:10.653                                         TEMPERATURE    50.200 DEG. C.
                                  INPUT SPECIES (MOLES)

                 H2O  = 5.55062+01                    HCL  = 3.64000-02
                 CAO  = 9.30000-03                    CO2  = 0.00000
                 MGO  = 0.00000                       N2O3 = 0.00000
                 NA2O = 1.30000-02                    N2O5 = 0.00000
                                                      SO2  = 7.00000-04
                                                      SO3  = 2.05000-03

           PH =  7.9130

           SUPERSATURATION ALLOWED

                          AQUEOUS SOLUTION EQUILIBRIA

          COMPONENT          MOLALITY            ACTIVITY     ACTIVITY COEFFICIENT

           H+                1.455-08            1.230-08            8.456-01
           H2O                                                       9.980-01
           H2SO3             2.250-11            2.269-11            1.009+00
           HSO3-             1.618-05            1.312-05            8.108-01
           HSO4-             1.766-09            1.432-09            8.108-01

           CA++              8.172-03            3.623-03            4.434-01
           CAOH+             5.621-07            4.558-07            8.108-01
           CASO3             5.509-04            5.559-04            1.009+00
           CAHSO3+           2.944-06            2.386-06            8.108-01
           CASO4             5.707-04            5.759-04            1.009+00

           NA+               2.560-02            2.124-02            8.297-01
           NAOH              2.552-08            2.576-08            1.009+00
           NASO3-            2.499-05            2.026-05            8.108-01
           NASO4-            8.907-05            7.220-05            8.108-01

           OH-               5.559-08            4.508-08            8.108-01
           CL-               3.839-02            3.093-02            8.058-01
           SO3--             1.048-04            4.529-05            4.321-01
           SO4--             1.400-03            5.594-04            3.997-01
          COMPONENT          MOLALITY        ACTIVITY PRODUCT  RELATIVE SATURATION




           CA(OH)2(S)        0.000               7.356-14            2.227-08
           CASO3(S)          0.000               1.640-07            2.448+00
           CASO4(S)          0.000               2.022-06            9.190-02

           PSO2 = 3.59645-11  ATM.

                      MOLECULAR WATER = 1.00035+00 KGS.

                    IONIC STRENGTH = 5.15537-02        RES. E.N. =   5.915-04
```

RUN NO. 70

DATE 4/27/76

$e^{-T/\tau}$ > 0.01

ANALYTICAL RESULTS

Species	Standards (mmoles/l)	Ca^{+} Feed (mmole/l)	SO_3^{-2} Feed (mmole/l)	Effluent (mmole/l)	Solids (mmole/g)
Ca^{+2}		39.2		8.59	7.61
Mg^{+2}					
Na^{+1}			43.5	22.3	
Cl^{-1}		76.9	0.	38.2	
CO_3^{-2}					7.41
Ts^{-2}			44.0	10.4	
SO_3^{-2}			20.1	0.73	6.62
SO_4^{-2}			23.9	9.67	0.826

OPERATING DATA

Time (min)	pH	Temp. ($^{\circ}C$)	SO_3^{-2} (mmole/l)	Solids Removal (ml/min)	Solids (wt%)	Solids (g)
125	8.12	31.8	0.73	200	0.094	2.61

COMPUTER RESULTS

Ionic Strength	Residual Electroneutrality	Relative Saturation			Mole Fraction	
		$CaSO_3 \cdot \frac{1}{2}H_2O$	$CaSO_4 \cdot 2H_2O$	$CaSO_4 \cdot \frac{1}{2}H_2O$	SO_3^{-2}	SO_4^{-2}
0.068	0.0028	2.25	0.30	0.14	0.89	0.11

REACTOR MATERIAL BALANCE CALCULATIONS

Run # 70 Date 4/27/76

INLET		A	B	Σ
Flow Rate (ml/min)		100	100	200
Ca^{+2}	(mmole/min)	3.92		3.92
Mg^{+2}	(mmole/min)			
Na_2^{+2}	(mmole/min)		4.35	4.35
Cl^{-1}	(mmole/min)	7.69		7.69
Ts	(mmole/min)			
SO_3^{-2}	(mmole/min)		2.01	2.01
SO_4^{-2}	(mmole/min)		2.39	2.39

OUTLET		Liquid	Solid	Σ
Flow Rate (ml/min)		200	0.188 (g/min)	
Ca^{+2}	(mmole/min)	1.72	1.43	3.15
Mg^{+2}	(mmole/min)			
Na_2^{+2}	(mmole/min)	4.46		4.46
Cl^{-1}	(mmole/min)	7.64		7.64
Ts	(mmole/min)			
SO_3^{-2}	(mmole/min)	0.146	1.24	1.39
SO_4^{-2}	(mmole/min)	1.93	0.155	2.08

PREC. RATE	mmole/min	mmole/g	grams/min
Solid			0.188
Ca^{+2}	2.20	7.61	0.289
SO_3^{-2}	1.86	6.62	0.281
SO_4^{-2}	0.46	0.826	0.557

SOLIDS MATERIAL BALANCE

Run No. 70

Date 4/27/76

	g/mmole	mmole/gram	g/gram
Ca^{++}	0.040	7.61	0.304
Mg^{++}	.024		
Na_2^{++}	.046		
Cl^-	.035		
$CO_3^=$	.060		
$SO_3^=$	.080	6.62	.530
$SO_4^=$	.096	.826	.079
$\frac{1}{2}H_2O$	.009	7.44	.067
			Σ .980

KINETIC RUN 70

```
03 MAY 76    16112111,412                                    TEMPERATURE    51,000 DEG, C,
                                  INPUT SPECIES (MOLES)

                  H2O  = 5,55062+01                 HCL  = 3,82000-02
                  CAO  = 8,59000-03                 CO2  = 0,00000
                  MGO  = 0,00000                    N2O3 = 0,00000
                  NA2O = 2,23000-02                 N2O5 = 0,00000
                                                    SO2  = 7,30000-04
                                                    SO3  = 9,67000-03

          PH =  8,1200


          SUPERSATURATION ALLOWED

                         AQUEOUS SOLUTION EQUILIBRIA

          COMPONENT          MOLALITY            ACTIVITY      ACTIVITY COEFFICIENT

           H+                9,071-09            7,585-09           8,362-01
           H2O                                                      9,984-01
           H2SO3             1,065-11            1,077-11           1,012+00
           HSO3-             1,357-05            1,075-05           7,922-01
           HSO4-             5,324-09            4,223-09           7,932-01

           CA++              6,221-03            2,535-03           4,074-01
           CAOH+             7,226-07            5,731-07           7,932-01
           CASO3             5,086-04            5,148-04           1,012+00
           CAHSO3+           1,787-06            1,418-06           7,932-01
           CASO4             1,855-03            1,877-03           1,012+00
            *
           NA+               4,383-02            3,527-02           8,046-01
           NAOH              7,527-08            7,617-08           1,012+00
           NASO3-            5,623-05            4,460-05           7,932-01
           NASO4-            6,934-04            5,499-04           7,932-01

           OH-               1,012-05            8,024-06           7,932-01
           CL-               3,819-02            3,002-02           7,862-01
           SO3--             1,496-04            5,890-05           3,938-01
           SO4--             7,119-03            2,544-03           3,574-01
          COMPONENT          MOLALITY         ACTIVITY PRODUCT  RELATIVE SATURATION




          CA(OH)2(S)         0,000               1,632-13           5,123-08
          CASO3(S)           0,000               1,492-07           2,252+00
          CASO4(S)           0,000               6,428-06           2,960-01
          PSO2 = 2,12403-11  ATM,

                        MOLECULAR WATER = 1,00034+00 KGS,

                      IONIC STRENGTH = 6,03777-02        RES, E,N, =   2,781-03
```

RUN NO. 71

DATE 4/27/76

$e^{-T/\tau}$ <0.01

ANALYTICAL RESULTS

Species	Standards (mmoles/l)	Ca^{+} Feed (mmole/l)	SO_3^{-2} Feed (mmole/l)	Effluent (mmole/l)	Solids (mmole/g)
Ca^{+2}		39.7		10.1	7.46
Mg^{+2}					
Na_2^{+1}			42.6	21.8	
Cl^{-1}		82.0	0.	42.0	
CO_3^{-2}			0.63	0.251	0.12
Ts^{-2}			44.1	11.3	7.22
SO_3^{-2}			21.0	2.24	6.56
SO_4^{-2}			23.1	9.06	0.865

OPERATING DATA

Time (min)	pH	Temp. (°C)	SO_3^{-2} (mmole/l)	Solids Removal (ml/min)	Solids (wt%)	Solids (g)
12.5	6.87	52.0	2.24	200	0.085	2.38

COMPUTER RESULTS

Ionic Strength	Residual Electroneutrality	Relative Saturation			Mole Fractio	
		$CaSO_3 \cdot \frac{1}{2}H_2O$	$CaSO_4 \cdot 2H_2O$	$CaSO_4 \cdot \frac{1}{2}H_2O$	SO_3^{-2}	SO_4^{-2}
0.071	-0.0004	5.30	0.30	0.14	0.884	0.116

REACTOR MATERIAL BALANCE CALCULATIONS

Run # 71 Date 4/27/76

INLET		A	B	Σ
Flow Rate (ml/min)		100	100	200
Ca^{+2}	(mmole/min)	3.97		3.97
Mg^{+2}	(mmole/min)			
Na_2^{+2}	(mmole/min)		4.26	4.26
Cl^{-1}	(mmole/min)	8.2		8.2
CO_3^{-2}	(mmole/min)		0.063	0.063
SO_3^{-2}	(mmole/min)		2.1	2.1
SO_4^{-2}	(mmole/min)		2.31	2.31

OUTLET		Liquid	Solid	Σ
Flow Rate (ml/min)		200	0.178 (g/min)	
Ca^{+2}	(mmole/min)	2.02	1.33	3.35
Mg^{+2}	(mmole/min)			
Na_2^{+2}	(mmole/min)	4.36		4.36
Cl^{-1}	(mmole/min)	8.4		8.4
CO_3^{-2}	(mmole/min)	0.050	0.021	0.071
SO_3^{-2}	(mmole/min)	0.448	1.17	1.162
SO_4^{-2}	(mmole/min)	1.82	0.15	1.97

PREC. RATE	mmole/min	mmole/g	grams/min
Solid			0.178
Ca^{+2}	1.95	7.46	0.261
SO_3^{-2}	1.65	6.56	0.252
SO_4^{-2}	0.49	0.865	0.566

SOLIDS MATERIAL BALANCE

Run No. 71

Date 4/27/76

	g/mmole	mmole/gram	g/gram
Ca^{++}	0.040	7.46	0.298
Mg^{++}	.024		
Na_2^{++}	.046		
Cl^-	.035		
$CO_3^=$	.060	.12	.007
$SO_3^=$	.080	6.56	.525
$SO_4^=$	.096	.865	.083
$\frac{1}{2}H_2O$	.009	7.42	.067
		Σ	

KINETIC RUN 71

```
03 MAY 76    16:12:12.072
                                                              TEMPERATURE    52.000 DEG. C.
                              INPUT SPECIES (MOLES)

                   H2O  = 5.55062+01               HCL  = 4.20000-02
                   CAO  = 1.01000-02               CO2  = 2.51000-04
                   MGO  = 0.00000                  N2O3 = 0.00000
                   NA2O = 2.18000-02               N2O5 = 0.00000
                                                   SO2  = 2.24000-03
                                                   SO3  = 9.35000-03

             PH =  6.8720

             SUPERSATURATION ALLOWED

                           AQUEOUS SOLUTION EQUILIBRIA

            COMPONENT          MOLALITY             ACTIVITY      ACTIVITY COEFFICIENT

             H+                1.616-07             1.349-07            8.349-01
             H2O                                                        9.903-01
             H2CO3             3.956-05             4.003-05            1.012+00
             HCO3-             1.933-04             1.526-04            7.895-01
             H2SO3             7.378-09             7.470-09            1.012+00
             HSO3-             5.214-04             4.116-04            7.895-01
             HSO4-             8.888-08             7.028-08            7.907-01

             CA++              6.928-03             2.788-03            4.025-01
             CAOH+             4.779-08             3.779-08            7.907-01
             CAHCO3+           1.194-05             9.439-06            7.907-01
             CACO3             4.673-07             4.731-07            1.012+00
             CASO3             1.201-03             1.216-03            1.012+00
             CAHSO3+           7.718-05             6.102-05            7.907-01
             CASO4             1.878-03             1.901-03            1.012+00

             NA+               4.284-02             3.437-02            8.023-01
             NAOH              4.369-09             4.423-09            1.012+00
             NAHCO3            5.104-06             5.165-06            1.012+00
             NACO3-            3.319-07             2.624-07            7.907-01
             NASO3-            1.181-04             9.340-05            7.907-01
             NASO4-            6.179-04             4.885-04            7.907-01




             OH-               6.047-07             4.781-07            7.907-01
             CL-               4.198-02             3.289-02            7.834-01
             CO3--             2.011-07             7.814-08            3.885-01
             SO3--             3.219-04             1.251-04            3.885-01
             SO4--             6.561-03             2.307-03            3.516-01
            COMPONENT          MOLALITY        ACTIVITY PRODUCT  RELATIVE SATURATION

             CA(OH)2(S)        0.000                6.374-16            2.047-10
             CACO3(S)          0.000                2.179-10            1.335-01
             CASO3(S)          0.000                3.464-07            5.296+00
             CASO4(S)          0.000                6.411-06            2.977-01

             PCO2 = 2.28616-03  ATM.
             PSO2 = 1.51731-08  ATM.

                          MOLECULAR WATER = 1.00037+00 KGS.

                        IONIC STRENGTH = 7.08060-02        RES. E.N. =  -4.160-04
```

RUN NO. E*-1

DATE 1/21/76

ANALYTICAL RESULTS

Species	Standards Percent Deviation	Initial Liquor (mmole/l)	Initial Solids (mmole/g)	Final Liquor (mmole/l)	Final Solids (mmole/l)
Ca^{+2}	+.2	10.55	7.60	13.0	7.10
Mg^{+2}	-.4	-----	----	----	----
Na^{+1}	+.2	10.0	----	10.0	0.05
Cl^{-1}	+.8	21.1	----	21.1	----
CO_3^{-2}		----	----	----	----
Ts^{-2}	+.2	10.0	7.42	13.3	7.10
SO_3^{-2}		0.	6.65	0.336	6.85
SO_4^{-2}	+.2	10.0	0.77	13.0	0.24

OPERATING DATA

Time (min)	pH	Temp. (°C)	SO_3^{-2} (mmole/l)	Solids (wt%)	Solids (g)
0	----	50	0.	0.357	2.001
7020	7.29	50	0.336	.304	1.700

COMPUTER RESULTS

Ionic Strength	Residual Electroneutrality	Relative Saturation $CaSO_3 \cdot \frac{1}{2}H_2O$	Relative Saturation $CaSO_4 \cdot 2H_2O$	Relative Saturation $CaSO_4 \cdot \frac{1}{2}H_2O$	Mole Fraction SO_3^{-2}	Mole Fraction SO_4^{-2}
0.0563	-0.001704	1.153	0.60	0.27	0.97	0.03

COMMENTS

K-9 solids with grinding.

Initial liquor concentrations normalized to final sodium and chloride concentrations.

RUN NO. E*-1

DATE 1/21/76

REACTOR MATERIAL BALANCE CALCULATIONS

Run # E*-1　　Date 1/21/76

INLET		Liquid	Solid	Σ
		560 ml	2.001 g	
Ca^{+2}	(mmole)	5.91	15.2	21.11
Mg^{+2}	(mmole)	----	----	-----
Na_2^{+2}	(mmole)	5.60	----	5.60
Cl^{-1}	(mmole)	11.82	----	11.82
T_s	(mmole)	5.60	14.85	20.45
SO_3^{-2}	(mmole)	0.	13.3	13.3
SO_4^{-2}	(mmole)	5.60	1.54	7.14

OUTLET		Liquid	Solid	Σ
		560 ml	1.700 g	
Ca^{+2}	(mmole)	7.28	12.07	19.35
Mg^{+2}	(mmole)	-----	-----	-----
Na_2^{+2}	(mmole)	5.60	-----	5.60
Cl^{-1}	(mmole)	11.82	-----	11.82
T_s	(mmole)	7.46	12.07	19.53
SO_3^{-2}	(mmole)	0.188	11.65	11.84
SO_4^{-2}	(mmole)	7.27	0.40	7.67

SOLIDS MATERIAL BALANCE

Run # E*-1 Date 1/21/76

	g/mmole	mmole/gram	g/gram
Ca^{+2}	.040	7.10	0.284
Mg^{+2}	.024	----	-----
Na_2^{+2}	.046	0.05	0.002
Cl^{-1}	.035	----	-----
CO_3^{-2}	.060	----	-----
SO_3^{-2}	.080	6.85	0.548
SO_4^{-2}	.096	0.24	0.023
$\frac{1}{2}H_2O$	.009	7.09*	0.064
			Σ 0.921

---

* Water concentration is based on the hypothesis that solid sulfate and sulfite each have one-half waters of hydration.

RUN NO. E*-2

DATE 1/21/76

ANALYTICAL RESULTS

Species	Standards Percent Deviation	Initial Liquor (mmole/l)	Initial Solids (mmole/g)	Final Liquor (mmole/l)	Final Solids (mmole/l)
Ca^{+2}	+.2	10.7	7.60	13.1	7.38
Mg^{+2}	-.4	----	----	----	----
Na^{+1}	+.2	10.3	----	10.3	0.03
Cl^{-1}	+.8	21.3	----	21.3	----
CO_3^{-2}		----	----	----	----
Ts^{-2}	+.2	10.3	7.42	13.44	7.19
SO_3^{-2}		0.	6.65	0.32	6.89
SO_4^{-2}	+.2	10.3	0.77	13.12	0.25

OPERATING DATA

Time (min)	pH	Temp. (°C)	SO_3^{-2} (mmole/l)	Solids (wt%)	Solids (g)
0	----	---	0.	0.345	2.001
7020	7.30	50	0.324	.296	1.717

COMPUTER RESULTS

Ionic Strength	Residual Electroneutrality	Relative Saturation $CaSO_3 \cdot \frac{1}{2}H_2O$	Relative Saturation $CaSO_4 \cdot 2H_2O$	Relative Saturation $CaSO_4 \cdot \frac{1}{2}H_2O$	Mole Fraction SO_3^{-2}	Mole Fraction SO_4^{-2}
0.0570	-0.00146	1.115	0.61	0.28	0.96	0.04

COMMENTS

K-9 solids without grinding.

Initial liquor concentrations normalized to final sodium and chloride concentrations.

RUN NO. E*-2
DATE 1/21/76

REACTOR MATERIAL BALANCE CALCULATIONS

Run # E*-2 Date 1/21/76

INLET		Liquid	Solid	Σ_{in}
		0.580 ml	2.001 g	mmole
Ca^{+2}	(mmole)	6.18	15.21	21.39
Mg^{+2}	(mmole)	----	-----	-----
Na_2^{+2}	(mmole)	5.95	-----	5.95
Cl^{-1}	(mmole)	12.36	-----	12.36
T_S	(mmole)	5.95	13.51	19.46
SO_3^{-2}	(mmole)	-----	13.31	13.31
SO_4^{-2}	(mmole)	5.95	1.54	7.49

OUTLET		Liquid	Solid	Σ_{out}
		0.580 ml	1.717 g	mmole
Ca^{+2}	(mmole)	7.60	12.67	20.27
Mg^{+2}	(mmole)	----	-----	-----
Na_2^{+2}	(mmole)	5.95	-----	5.95
Cl^{-1}	(mmole)	12.36	-----	12.36
T_S	(mmole)	7.80	12.34	20.14
SO_3^{-2}	(mmole)	0.188	11.83	12.02
SO_4^{-2}	(mmole)	7.61	0.43	8.04

SOLIDS MATERIAL BALANCE

Run # E*-2 Date 1/21/76

	g/mmole	mmole/gram	g/gram
Ca^{+2}	.040	7.38	0.295
Mg^{+2}	.024	-----	-----
Na_2^{+2}	.046	0.03	0.001
Cl^{-1}	.035	-----	-----
CO_3^{-2}	.060	-----	-----
SO_3^{-2}	.080	6.89	0.551
SO_4^{-2}	.096	0.25	0.024
$\frac{1}{2}H_2O$	.009	7.14*	0.064
			Σ 0.935

---

* Water concentration is based on the hypothesis that the solid sulfate and sulfite each have one-half waters of hydration.

RUN NO. E*-3

DATE 1/21/76

ANALYTICAL RESULTS

Species	Standards Percent Deviation	Initial Liquor (mmole/l)	Initial Solids (mmole/g)	Final Liquor (mmole/l)	Final Solids (mmole/l)
Ca^{+2}	+.2	10.8	7.15	12.4	7.28
Mg^{+2}	-.4	----	0.03	0.01	----
Na^{+1}	+.2	10.3	0.04	10.25	0.03
Cl^{-1}	+.8	21.6	----	21.6	----
CO_3^{-2}		----	----	----	----
Ts^{-2}	+.2	10.3	6.75	12.7	7.35
SO_3^{-2}		0.	5.65	0.37	6.55
SO_4^{-2}	+.2	10.3	1.11	12.3	0.78

OPERATING DATA

Time (min)	pH	Temp. (°C)	SO_3^{-2} (mmole/l)	Solids (wt%)	Solids (g)
0	--	--	0.	0.207	1.199
7020	7.38	50	0.369	0.170	0.987

COMPUTER RESULTS

Ionic Strength	Residual Electroneutrality	Relative Saturation			Mole Fraction	
		$CaSO_3 \cdot \frac{1}{2}H_2O$	$CaSO_4 \cdot 2H_2O$	$CaSO_4 \cdot \frac{1}{2}H_2O$	SO_3^{-2}	SO_4^{-2}
0.0553	-0.00161	1.279	0.56	0.25	0.89	0.11

COMMENTS

K-38 solids used with grinder.

Initial liquor concentrations normalized to final sodium and chloride concentrations.

RUN NO. E*-3

DATE 1/21/76

REACTOR MATERIAL BALANCE CALCULATIONS

Run # E*-3 Date 1/21/76

INLET		Liquid	Solid	Σ_{in}
		580 ml	1.19943 g	mmole
Ca^{+2}	(mmole)	6.26	8.58	14.84
Mg^{+2}	(mmole)	-----	0.03	0.03
Na_2^{+2}	(mmole)	5.95	0.05	6.00
Cl^{-1}	(mmole)	12.52	-----	12.57
T_s	(mmole)	5.95	8.09	14.04
SO_3^{-2}	(mmole)	-----	6.78	6.78
SO_4^{-2}	(mmole)	5.95	1.33	7.28

OUTLET		Liquid	Solid	Σ_{out}
		580 ml	0.987 g	mmole
Ca^{+2}	(mmole)	7.19	7.19	14.38
Mg^{+2}	(mmole)	0.003	-----	0.003
Na_2^{+2}	(mmole)	5.95	0.03	5.98
Cl^{-1}	(mmole)	12.53	-----	12.53
T_s	(mmole)	-----	-----	-----
SO_3^{-2}	(mmole)	0.214	6.46	6.67
SO_4^{-2}	(mmole)	7.35	0.774	8.12

SOLIDS MATERIAL BALANCE

Run # E*-3 Date 1/21/76

	g/mmole	mmole/gram	g/gram
Ca^{+2}	.040	7.28	0.291
Mg^{+2}	.024	-----	-----
Na_2^{+2}	.046	0.03	0.001
Cl^{-1}	.035	-----	-----
CO_3^{-2}	.060	-----	-----
SO_3^{-2}	.080	6.55	0.524
SO_4^{-2}	.096	0.78	0.75
$\frac{1}{2}H_2O$	.009	7.33*	0.066
			Σ 0.957

---

* Water concentration is based on the hypothesis that solid sulfate and sulfite each have one-half waters of hydration.

RUN NO. E*-4

DATE 1/21/76

ANALYTICAL RESULTS

Species	Standards Percent Deviation	Initial Liquor (mmole/l)	Initial Solids (mmole/g)	Final Liquor (mmole/l)	Final Solids (mmole/l)
Ca^{+2}	+.2	16.4	7.29	17.3	7.34
Mg^{+2}	-.4	----	0.04	0.182	----
Na^{+1}	+.2	16.2	0.05	16.2	0.03
Cl^{-1}	+.8	32.8	----	32.8	----
CO_3^{-2}		----	----	----	----
Ts^{-2}	+.2	16.2	6.99	17.9	7.24
SO_3^{-2}		0.	6.06	0.39	6.22
SO_4^{-2}	+.2	16.2	1.08	17.5	1.05

OPERATING DATA

Time (min)	pH	Temp. (°C)	SO_3^{-2} (mmole/l)	Solids (wt%)	Solids (g)
0	---	--	0.	0.351	2.000
7020	7.31	50	0.392	0.321	1.827

COMPUTER RESULTS

Ionic Strength	Residual Electroneutrality	Relative Saturation $CaSO_3 \cdot \frac{1}{2}H_2O$	Relative Saturation $CaSO_4 \cdot 2H_2O$	Relative Saturation $CaSO_4 \cdot \frac{1}{2}H_2O$	Mole Fraction SO_3^{-2}	Mole Fraction SO_4^{-2}
0.0799	-0.00137	1.380	0.82	0.37	0.86	0.14

COMMENTS

K-41 solids with grinder.

Initial liquor concentrations normalized to final sodium and chloride concentrations.

RUN NO. E*-4

DATE 1/21/76

REACTOR MATERIAL BALANCE CALCULATIONS

Run # E*-4 Date 1/21/76

INLET		Liquid	Solid	Σ_{in}
		570 ml	2.00014 g	mmole
Ca^{+2}	(mmole)	9.35	14.58	23.93
Mg^{+2}	(mmole)	-----	0.104	0.10
Na_2^{+2}	(mmole)	9.21	0.08	9.29
Cl^{-1}	(mmole)	18.70	-----	18.70
T_s	(mmole)	9.21	13.98	23.19
SO_3^{-2}	(mmole)	-----	12.12	12.12
SO_4^{-2}	(mmole)	9.21	2.16	11.37

OUTLET		Liquid	Solid	Σ_{out}
		570 ml	1.827 g	mmole
Ca^{+2}	(mmole)	9.86	13.41	23.27
Mg^{+2}	(mmole)	0.10	-----	0.10
Na_2^{+2}	(mmole)	9.21	0.055	9.27
Cl^{-1}	(mmole)	18.70	-----	18.70
T_s	(mmole)	10.22	13.23	23.45
SO_3^{-2}	(mmole)	0.22	11.36	11.58
SO_4^{-2}	(mmole)	10.00	1.92	11.92

SOLIDS MATERIAL BALANCE

Run # E*-4 Date 1/21/76

	g/mmole	mmole/gram	g/gram
Ca^{+2}	.040	7.34	0.294
Mg^{+2}	.024	----	-----
Na_2^{+2}	.046	0.03	0.001
Cl^{-1}	.035	-----	-----
CO_3^{-2}	.060	-----	-----
SO_3^{-2}	.080	6.22	0.498
SO_4^{-2}	.096	1.05	0.101
$\frac{1}{2}H_2O$	.009	7.27 *	0.065
			Σ 0.959

---

* Water concentration is based on the hypothesis that the solid sulfate and sulfite each have one-half waters of hydration.

RUN NO. E*-5

DATE 1/21/76

ANALYTICAL RESULTS

Species	Standards Percent Deviation	Initial Liquor (mmole/l)	Initial Solids (mmole/g)	Final Liquor (mmole/l)	Final Solids (mmole/l)
Ca^{+2}	+.2	16.2	7.29	16.6	7.30
Mg^{+2}	-.4	----	0.05	0.18	----
Na^{+1}	+.2	16.3	0.04	16.3	0.03
Cl^{-1}	+.8	32.3	----	32.3	----
CO_3^{-2}		----	----	----	----
Ts^{-2}	+.2	16.3	6.99	17.5	7.39
SO_3^{-2}		0.	6.06	0.41	6.25
SO_4^{-2}	+.2	16.3	1.08	17.1	1.12

OPERATING DATA

Time (min)	pH	Temp. (°C)	SO_3^{-2} (mmole/l)	Solids (wt%)	Solids (g)
0	----	--	0.	0.351	2.000
7020	7.33	50	0.406	0.319	1.820

COMPUTER RESULTS

Ionic Strength	Residual Electroneutrality	Relative Saturation $CaSO_3 \cdot \frac{1}{2}H_2O$	Relative Saturation $CaSO_4 \cdot 2H_2O$	Relative Saturation $CaSO_4 \cdot \frac{1}{2}H_2O$	Mole Fraction SO_3^{-2}	Mole Fraction SO_4^{-2}
0.0781	-0.00164	1.425	0.78	0.35	0.85	0.15

COMMENTS

K-41 solids with grinding.

Initial liquor concentrations normalized to final sodium and chloride concentrations.

RUN NO. E*-5
DATE 1/21/76

REACTOR MATERIAL BALANCE CALCULATIONS

Run # E*-5 Date 1/21/76

INLET		Liquid	Solid	Σ_{in}
		570 ml	2.00014 g	mmole
Ca^{+2}	(mmole)	9.21	14.58	23.79
Mg^{+2}	(mmole)	-----	0.10	0.10
Na_2^{+2}	(mmole)	9.12	0.08	9.20
Cl^{-1}	(mmole)	18.42	-----	18.42
T_s	(mmole)	9.12	13.98	23.10
SO_3^{-2}	(mmole)	-----	12.12	12.12
SO_4^{-2}	(mmole)	9.12	2.16	11.28

OUTLET		Liquid	Solid	Σ_{out}
		570 ml	1.820 g	mmole
Ca^{+2}	(mmole)	9.46	13.29	22.75
Mg^{+2}	(mmole)	0.10	-----	0.10
Na_2^{+2}	(mmole)	9.26	0.055	9.32
Cl^{-1}	(mmole)	18.41	-----	18.41
T_s	(mmole)	9.96	13.45	23.41
SO_3^{-2}	(mmole)	0.23	11.38	11.61
SO_4^{-2}	(mmole)	9.72	2.04	11.76

SOLIDS MATERIAL BALANCE

Run # E*-5 Date 1/21/76

	g/mmole	mmole/gram	g/gram
Ca^{+2}	.040	7.30	0.292
Mg^{+2}	.024	----	-----
Na_2^{+2}	.046	0.03	0.001
Cl^{-1}	.035	----	-----
CO_3^{-2}	.060	----	-----
SO_3^{-2}	.080	6.25	0.500
SO_4^{-2}	.096	1.12	0.108
$\frac{1}{2}H_2O$	.009	7.37 *	0.066
			Σ 0.967

---

* Water concentration is based on the hypothesis that the solid sulfate and sulfite each have one-half waters of hydration.

RUN NO. E*-6

DATE 1/21/76

ANALYTICAL RESULTS

Species	Standards Percent Deviation	Initial Liquor (mmole/l)	Initial Solids (mmole/g)	Final Liquor (mmole/l)	Final Solids (mmole/l)
Ca^{+2}	+.2	16.4	6.96	17.1	6.63
Mg^{+2}	-.4	----	----	----	----
Na^{+1}	+.2	16.3	----	16.3	0.03
Cl^{-1}	+.8	32.8	----	32.8	----
CO_3^{-2}		----	----	----	----
Ts^{-2}	+.2	16.3	7.06	18.0	6.85
SO_3^{-2}		0.	5.89	0.32	6.09
SO_4^{-2}	+.2	16.3	0.74	17.7	0.73

OPERATING DATA

Time (min)	pH	Temp. (°C)	SO_3^{-2} (mmole/l)	Solids (wt%)	Solids (g)
0	----	--	0.	0.213	1.216
7020	7.38	50	0.317	0.179	1.022

COMPUTER RESULTS

Ionic Strength	Residual Electroneutrality	Relative Saturation $CaSO_3\cdot\frac{1}{2}H_2O$	Relative Saturation $CaSO_4\cdot 2H_2O$	Relative Saturation $CaSO_4\cdot\frac{1}{2}H_2O$	Mole Fraction SO_3^{-2}	Mole Fraction SO_4^{-2}
0.0799	-0.00208	1.127	0.82	C.37	0.89	0.11

COMMENTS

K-19 (0.947 g) and K-20 (0.270 g) were mixed and used in these equilibrium studies with grinding.

Initial liquor concentrations normalized to final sodium and chloride concentrations.

RUN NO. E*-6
DATE 1/21/76

REACTOR MATERIAL BALANCE CALCULATIONS

Run # E*-6 Date 1/21/76

INLET		Liquid	Solid	Σ_{in}
		570 ml	1.21568 g	mmole
Ca^{+2}	(mmole)	9.35	8.46	17.81
Mg^{+2}	(mmole)	-----	-----	-----
Na_2^{+2}	(mmole)	9.26	-----	9.26
Cl^{-1}	(mmole)	18.70	-----	18.70
T_s	(mmole)	9.26	8.58	17.84
SO_3^{-2}	(mmole)	-----	7.16	7.16
SO_4^{-2}	(mmole)	9.26	0.90	10.16

OUTLET		Liquid	Solid	Σ_{out}
		570 ml	1.022 g	mmole
Ca^{+2}	(mmole)	9.75	6.78	16.53
Mg^{+2}	(mmole)	-----	-----	-----
Na_2^{+2}	(mmole)	9.26	0.03	9.29
Cl^{-1}	(mmole)	18.70	-----	18.70
T_s	(mmole)	10.26	7.00	17.26
SO_3^{-2}	(mmole)	0.18	6.22	6.40
SO_4^{-2}	(mmole)	10.08	0.74	10.82

SOLIDS MATERIAL BALANCE

Run # E*-6   Date 1/21/76

	g/mmole	mmole/gram	g/gram
Ca^{+2}	.040	6.63	0.265
Mg^{+2}	.024	----	-----
Na_2^{+2}	.046	0.03	0.001
Cl^{-1}	.035	----	-----
CO_3^{-2}	.060	-----	-----
SO_3^{-2}	.080	6.09	0.487
SO_4^{-2}	.096	0.73	0.070
$\frac{1}{2}H_2O$	.009	6.82 *	0.061
			Σ 0.884

---

* Water concentration is based on the hypothesis that the solid sulfate and sulfite each have one-half waters of hydration.

RUN NO. E*-7

DATE 2/11/75

ANALYTICAL RESULTS

Species	Standards (% Deviation)	INITIAL Liquid (mmole/l)	INITIAL Solid (mmole/g)	FINAL Liquor (mmole/l)	FINAL Solids (mmole/g)
Ca^{+2}	-.1	0	7.58	1.16	7.55
Mg^{+2}	0	0		0	--
Na_2^{+1}	-.8	0		.30	.05
Cl^{-1}	.3	0		0	--
CO_3^{-2}	--	0		--	--
Ts^{-2}	1.0	0		1.00	7.20
SO_3^{-2}	--	0	7.50	.53	7.41
SO_4^{-2}	1.0	0	.08	.47	.07

OPERATING DATA

Time (hr)	pH	Temp. (°C)	SO_3^{-2} (mmole/l)	Solids (wt%)	Solids (g)
0					2.000
288	7.51	49.3	.53		1.586

COMPUTER RESULTS

Ionic Strength	Residual Electroneutrality	Relative Saturation $CaSO_3 \cdot \frac{1}{2}H_2O$	Relative Saturation $CaSO_4 \cdot 2H_2O$	Relative Saturation $CaSO_4 \cdot \frac{1}{2}H_2O$	Mole Fraction SO_3^{-2}	Mole Fraction SO_4^{-2}
.0032	.0010	1.20	.009	.004	.99	.01

COMMENTS

$CaSO_3 \cdot \frac{1}{2}H_2O$ seed crystals added to boiled DI H_2O.

RUN NO. E*-7

DATE 2/11/76

REACTOR MATERIAL BALANCE CALCULATIONS

Run # E*-7 Date 2/11/76

INLET		Liquid	Solid	Σ
Flow Rate		560 ml	2.000 g	
Ca^{+2}	(mmole)	----	15.2	15.2
Mg^{+2}	(mmole)	----	----	----
Na_2^{+2}	(mmole)	----	----	----
Cl^{-1}	(mmole)	----	----	----
T_s	(mmole)	----	15.2	15.2
SO_3^{-2}	(mmole)	----	15.0	15.0
SO_4^{-2}	(mmole)	----	.2	.2

OUTLET		Liquid	Solid	Σ
Flow Rate		560 ml	1.59 g	
Ca^{+2}	(mmole)	0.65	12.0	12.7
Mg^{+2}	(mmole)	----	----	----
Na_2^{+2}	(mmole)	.17	.08	.25
Cl^{-1}	(mmole)	----	----	----
T_s	(mmole)	.56	11.5	12.1
SO_3^{-2}	(mmole)	.30	11.8	12.1
SO_4^{-2}	(mmole)	.26	.11	.4

SOLIDS MATERIAL BALANCE

Run # E#-7 Date 2/11/76

	g/mmole	mmole/gram	g/gram
Ca^{+2}	.040	7.55	.302
Mg^{+2}	.024	--	--
Na_2^{+2}	.046	.05	.002
Cl^{-1}	.035	--	--
CO_3^{-2}	.060	--	--
SO_3^{-2}	.080	7.41	.593
SO_4^{-2}	.096	.067	.006
$\frac{1}{2}H_2O$	.009	7.47	.067

Σ .970

EQUILIBRIUM RUN 7

```
03 MAR 76    14:19:12.842
                              INPUT SPECIES (MOLES)          TEMPERATURE    49.300 DEG. C.

              H2O  = 5.55082+01                 HCL  = 0.00000
              CAO  = 1.14000-03                 CO2  = 0.00000
              MGO  = 0.00000                    N2O3 = 0.00000
              NA2O = 3.00000-04                 N2O5 = 0.00000
                                                SO2  = 5.30000-04
                                                SO3  = 4.70000-04

      PH = 7.5100

      SUPERSATURATION ALLOWED

                    AQUEOUS SOLUTION EQUILIBRIA
      COMPONENT         MOLALITY          ACTIVITY        ACTIVITY COEFFICIENT
      H+                3.283-08          3.090-08              9.410-01
      H2O                                                       1.000+00
      H2SO3             3.543-10          3.545-10              1.001+00
      HSO3-             9.598-05          8.985-05              9.360-01
      HSO4-             2.109-09          1.977-09              9.375-01

      CA++              8.329-04          6.457-04              7.752-01
      CAOH+             3.292-08          3.086-08              9.375-01
      CASO3             2.738-04          2.740-04              1.001+00
      CASO4             5.719-05          5.723-05              1.001+00

      NA+               5.973-04          5.600-04              9.380-01
      NAOH              2.579-10          2.578-10              1.001+00
      NASO3-            1.499-06          1.405-06              9.375-01
      NASO4-            1.145-06          1.073-06              9.375-01

      OH-               1.816-06          1.703-06              9.375-01
      SO3--             1.619-04          1.252-04              7.740-01
      SO4--             4.117-04          3.155-04              7.668-01
     COMPONENT          MOLALITY       ACTIVITY PRODUCT   RELATIVE SATURATION
      CA(OH)2(S)        0.000             1.870-15              5.547-12




      CASO3(S)          0.000             8.078-08              1.198+00
      CASO4(S)          0.000             2.041-07              9.213-03
      PCO2 = 6.30677-10  ATM.

                 MOLECULAR WATER = 9.99990-01 KGS.

               IONIC STRENGTH = 3.15977-03          RES. E.N. =   1.014-03
```

RUN NO. E*-8
DATE 2/11/76

ANALYTICAL RESULTS

		INITIAL		FINAL	
Species	Standards (% Deviation)	Liquid (mmole/l)	Solid (mmole/g)	Liquor (mmole/l)	Solids (mmole/g)
Ca^{+2}	-.1	9.5	7.58	11.4	7.44
Mg^{+2}	0			--	--
Na_2^{+1}	-.8	9.5		11.1	.06
Cl^{-1}	.3	19		20.6	--
CO_3^{-2}	--			--	--
Ts^{-2}	1.0	9.5		11.3	7.02
SO_3^{-2}	--		7.50	.322	7.30
SO_4^{-2}	1.0	9.5	.08	11.0	.10

OPERATING DATA

Time (hr)	pH	Temp. (°C)	SO_3^{-2} (mmole/l)	Solids (wt%)	Solids (g)
0					2.000
288	7.08	50	.322		1.592

COMPUTER RESULTS

		Relative Saturation			Mole Fraction	
Ionic Strength	Residual Electroneutrality	$CaSO_3 \cdot \frac{1}{2}H_2O$	$CaSO_4 \cdot 2H_2O$	$CaSO_4 \cdot \frac{1}{2}H_2O$	SO_3^{-2}	SO_4^{-2}
.0529	.0018	1.00	.49	.22	.99	.01

COMMENTS

RUN NO. E*-8
DATE 2/11/76

REACTOR MATERIAL BALANCE CALCULATIONS

Run # E*-8 Date 2/11/76

INLET		Liquid	Solid	Σ
Flow Rate		580 ml	2.000 g	
Ca^{+2}	(mmole)	5.51	15.2	20.7
Mg^{+2}	(mmole)	---	----	----
Na_2^{+2}	(mmole)	5.51	----	5.51
Cl^{-1}	(mmole)	11.0	----	11.0
T_s	(mmole)	5.51	15.2	20.7
SO_3^{-2}	(mmole)	----	15.0	15.0
SO_4^{-2}	(mmole)	5.51	.2	5.7

OUTLET		Liquid	Solid	Σ
Flow Rate		580 ml	1.59 g	
Ca^{+2}	(mmole)	6.61	11.8	18.4
Mg^{+2}	(mmole)	----	----	----
Na_2^{+2}	(mmole)	6.44	.1	6.54
Cl^{-1}	(mmole)	11.95	----	11.95
T_s	(mmole)	6.55	11.2	17.7
SO_3^{-2}	(mmole)	.19	11.61	11.8
SO_4^{-2}	(mmole)	6.38	.16	6.5

SOLIDS MATERIAL BALANCE

Run # E#-8 Date 2/11/76

	g/mmole	mmole/gram	g/gram
Ca^{+2}	.040	7.44	.298
Mg^{+2}	.024	--	--
Na_2^{+2}	.046	.06	.003
Cl^{-1}	.035	--	--
CO_3^{-2}	.060	--	--
SO_3^{-2}	.080	7.30	.584
SO_4^{-2}	.096	.10	.010
$\frac{1}{2}H_2O$	.009	7.40	.067
			Σ .961

EQUILIBRIUM RUN 8

```
03 MAR 76    14:15:14.045                                          TEMPERATURE    50.000 DEG. C.
                                     INPUT SPECIES (MOLES)

                    H2O  = 5.55062+01                 HCL  = 2.00000-02
                    CAO  = 1.14000-02                 CO2  = 0.00000
                    MGO  = 0.00000                    N2O3 = 0.00000
                    NA2O = 1.11020-02                 N2O5 = 0.00000
                                                      SO2  = 3.22000-04
                                                      SO3  = 1.10000-02

         PH =  7.080

         SUPERSATURATION ALLOWED

                       AQUEOUS SOLUTION EQUILIBRIA

       COMPONENT          MOLALITY            ACTIVITY      ACTIVITY COEFFICIENT

        H+                9.442-08            8.314-08            8.805-01
        H2O                                                       9.990-01
        H2SO3             3.045-12            3.041-12            1.000+00
        HSO3-             4.313-05            3.853-05            8.094-01
        HSO4-             6.377-08            5.161-08            8.093-01

        CA++              8.144-03            3.590-03            4.408-01
        CAOH+             8.148-08            6.594-08            8.093-01
        CASO3             2.257-04            2.271-04            1.000+00
        CASO4             3.025-03            3.053-03            1.000+00

        NA+               2.178-02            1.765-02            8.105-01
        NAOH              3.137-09            3.196-09            1.000+00
        NASO3-            6.256-08            5.061-08            8.093-01
        NASO4-            4.022-04            3.254-04            8.093-01

        OH-               5.641-07            4.560-07            8.093-01
        CL-               2.060-02            1.657-02            8.044-01
        SO3--             4.359-05            1.871-05            4.292-01
        SO4--             7.571-03            3.002-03            3.965-01

       COMPONENT          MOLALITY        ACTIVITY PRODUCT  RELATIVE SATURATION




        CA(OH)2(S)        0.000               1.959-15            4.697-10
        CASO3(S)          0.000               6.714-08            1.001+00
        CASO4(S)          0.000               1.276-05            4.881-01

        PSO2 = 7.24442-10  ATM.

                    MOLECULAR WATER = 1.00018+00 KGS.

                 IONIC STRENGTH = 5.29430-02        RES. E.N. =   1.799-03
```

RUN NO. E*-9

DATE 2/11/76

ANALYTICAL RESULTS

Species	Standards (% Deviation)	INITIAL Liquid (mmole/l)	INITIAL Solid (mmole/g)	FINAL Liquor (mmole/l)	FINAL Solids (mmole/g)
Ca^{+2}	-.1	14	7.58	16.6	7.43
Mg^{+2}	0	419		419	.02
Na_2^{+1}	-.8			--	.05
Cl^{-1}	.3	607		607	--
CO_3^{-2}	--			--	--
Ts^{-2}	1.0	130		146	7.03
SO_3^{-2}	--		7.50	3.23	7.30
SO_4^{-2}	1.0	130	.08	143	.06

OPERATING DATA

Time (hr)	pH	Temp. (°C)	SO_3^{-2} (mmole/l)	Solids (wt%)	Solids (g)
0					2.000
288	7.20	49	3.23		1.318

COMPUTER RESULTS

Ionic Strength	Residual Electroneutrality	Relative Saturation			Mole Fraction	
		$CaSO_3 \cdot \frac{1}{2}H_2O$	$CaSO_4 \cdot 2H_2O$	$CaSO_4 \cdot \frac{1}{2}H_2O$	SO_3^{-2}	SO_4^{-2}
1.09	-.03	1.27	.57	.25	.99	.01

COMMENTS

RUN NO. E*-9

DATE 2/11/76

REACTOR MATERIAL BALANCE CALCULATIONS

Run # E*-9 Date 2/11/76

INLET		Liquid	Solid	Σ
Flow Rate		580 ml	2.000 g	
Ca^{+2}	(mmole)	8.12	15.2	23.3
Mg^{+2}	(mmole)	243.	----	243.
Na_2^{+2}	(mmole)	----	----	----
Cl^{-1}	(mmole)	352.	----	352.
T_S	(mmole)	75.4	15.2	90.4
SO_3^{-2}	(mmole)	----	15.0	15.
SO_4^{-2}	(mmole)	75.4	.2	75.6

OUTLET		Liquid	Solid	Σ
Flow Rate		580 ml	1.32 g	
Ca^{+2}	(mmole)	9.63	9.81	19.4
Mg^{+2}	(mmole)	243.	----	243.
Na_2^{+2}	(mmole)	----	.07	.07
Cl^{-1}	(mmole)	352.	----	352.
T_S	(mmole)	85.	9.28	94.3
SO_3^{-2}	(mmole)	1.87	9.64	11.5
SO_4^{-2}	(mmole)	83.	.08	83.1

SOLIDS MATERIAL BALANCE

Run # E#-9 Date 2/11/76

	g/mmole	mmole/gram	g/gram
Ca^{+2}	.040	7.43	.297
Mg^{+2}	.024	.02	.001
Na_2^{+2}	.046	.05	.002
Cl^{-1}	.035	--	--
CO_3^{-2}	.060	--	--
SO_3^{-2}	.080	7.30	.584
SO_4^{-2}	.096	.06	.006
$\frac{1}{2}H_2O$	.009	7.36	.066

Σ .956

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EQUILIBRIUM RUN 9

```
03 MAR 76    14115115.481                                    TEMPERATURE    40.000 DEG. C.
                                 INPUT SPECIES (MOLES)

                  H2O  = 5.55062+01              HCL  = 6.07000-01
                  CAO  = 1.60000-02              CO2  = 0.00000
                  MGO  = 4.19444-01              N2O3 = 0.00000
                  NA2O = 0.00000                 N2O5 = 0.00000
                                                 SO2  = 3.23000-03
                                                 SO3  = 1.43000-01

          PH =  7.2001

          SUPERSATURATION ALLOWED

                      AQUEOUS SOLUTION EQUILIBRIA

        COMPONENT          MOLALITY          ACTIVITY     ACTIVITY COEFFICIENT

         H+                5.579-08          6.348-08          1.131+00
         H2O                                                   9.824-01
         H2SO3             2.714-10          3.286-10          1.211+00
         HSO3-             6.459-05          4.154-05          6.458-01
         HSO4-             6.521-09          5.445-09          7.963-01

         CA++              1.324-02          3.053-03          2.306-01
         CAOH+             8.529-09          6.797-09          7.963-01
         CASO3             2.398-04          2.903-04          1.211+00
         CASO4             3.033-03          3.672-03          1.211+00

         MG++              3.283-01          9.626-02          2.932-01
         MGOH+             5.920-05          4.714-05          7.963-01
         MGSO3             2.593-03          3.200-03          1.211+00
         MGSO4             9.954-02          1.237-01          1.211+00

         OH-               1.098-06          8.747-07          7.963-01
         CL-               6.037-01          3.524-01          5.838-01
         SO3--             2.115-04          2.845-05          1.345-01
         SO4--             5.395-02          4.340-03          8.046-02

        COMPONENT          MOLALITY       ACTIVITY PRODUCT  RELATIVE SATURATION




        CA(OH)2(S)         0.000             1.977-15          5.825-10
        CASO3(S)           0.000             8.464-08          1.274+00
        CASO4(S)           0.000             1.272-05          5.718-01
        MG(OH)2(S)         0.000             5.234-14          6.549-03
        MGSO3(S)           0.000             2.566-06          4.429-02

        PSO2 = 6.48059-10  ATM.

                    MOLECULAR WATER = 1.00547+00 KGS.

                  IONIC STRENGTH = 1.00257+00        RES. E.N. =  -2.809-02
```

RUN NO. E*-10

DATE 2/11/76

ANALYTICAL RESULTS

Species	Standards (% Deviation)	INITIAL Liquid (mmole/l)	INITIAL Solid (mmole/g)	FINAL Liquor (mmole/l)	FINAL Solids (mmole/g)
Ca^{+2}	-.1	18	7.29	23.7	6.86
Mg^{+2}	0	487	.05	479	.08
Na^{+1}	-.8		.04	--	.07
Cl^{-1}	.3	636		654	--
CO$_3^{-2}$	--			--	--
Ts^{-2}	1.0	187	6.99	197	6.53
SO$_3^{-2}$	--		6.06	3.61	5.80
SO$_4^{-2}$	1.0	187	1.08	193	1.05

OPERATING DATA

Time (hr)	pH	Temp. (^{o}C)	SO$_3^{-2}$ (mmole/l)	Solids (wt%)	Solids (g)
0					.9383
288	7.11	48.9	3.61		.4162

COMPUTER RESULTS

Ionic Strength	Residual Electroneutrality	Relative Saturation CaSO$_3\cdot\frac{1}{2}$H$_2$O	Relative Saturation CaSO$_4\cdot$2H$_2$O	Relative Saturation CaSO$_4\cdot\frac{1}{2}$H$_2$O	Mole Fraction SO$_3^{-2}$	Mole Fraction SO$_4^{-2}$
1.22	-.042	1.78	.98	.43	.85	.15

COMMENTS

RUN NO. E*-10

DATE 2/11/76

REACTOR MATERIAL BALANCE CALCULATIONS

Run # E*-10   Date 2/11/76

INLET		Liquid	Solid	Σ
Flow Rate		570 ml	0.938 g	
Ca^{+2}	(mmole)	10.3	6.84	17.1
Mg^{+2}	(mmole)	278.	.05	278.
Na_2^{+2}	(mmole)	----	.04	.04
Cl^{-1}	(mmole)	369.	----	369.
T_s	(mmole)	107.	6.56	114.
SO_3^{-2}	(mmole)	----	5.68	5.68
SO_4^{-2}	(mmole)	107.	1.01	108.

OUTLET		Liquid	Solid	Σ
Flow Rate		570 ml	0.416 g	
Ca^{+2}	(mmole)	13.51	2.85	16.4
Mg^{+2}	(mmole)	273.	----	273.
Na_2^{+2}	(mmole)	----	.03	.03
Cl^{-1}	(mmole)	373.	----	373.
T_s	(mmole)	113	2.72	116.
SO_3^{-2}	(mmole)	2.06	2.41	4.47
SO_4^{-2}	(mmole)	110.	.44	110.

SOLIDS MATERIAL BALANCE

Run # E#-10 Date 2/11/76

	g/mmole	mmole/gram	g/gram
Ca^{+2}	.040	6.86	.274
Mg^{+2}	.024	.08	.002
Na_2^{+2}	.046	.07	.003
Cl^{-1}	.035	--	--
CO_3^{-2}	.060	--	--
SO_3^{-2}	.080	5.80	.464
SO_4^{-2}	.096	1.05	.101
$\frac{1}{2}H_2O$	.009	6.85	.062
			Σ .906

EQUILIBRIUM RUN 10

```
03 MAR 76    14115314.748                                   TEMPERATURE    48.000 DEG. C.
                              INPUT SPECIES (MOLES)

                 H2O  = 5.55062+01            HCL  = 6.54000-01
                 CAO  = 2.37600-02            CO2  = 0.00000
                 MGO  = 4.79000-01            N2O3 = 0.00000
                 NA2O = 0.00000               N2O5 = 0.00000
                                              SO2  = 3.61000-03
                                              SO3  = 1.03000-01

          PH =  7.1121

          SUPERSATURATION ALLOWED

                        AQUEOUS SOLUTION EQUILIBRIA

          COMPONENT          MOLALITY          ACTIVITY      ACTIVITY COEFFICIENT

           H+                6.590-08          7.701-08            1.164+00
           H2O                                                     9.841-01
           H2SO3             4.011-10          4.964-10            1.237+00
           HSO3-             9.597-05          5.118-05            5.593-01
           HSO4-             1.004-07          8.255-08            8.223-01

           CA++              1.812-02          4.263-03            2.353-01
           CAOH+             9.313-08          7.658-08            8.223-01
           CASO3             3.279-04          4.055-04            1.237+00
           CASO4             5.114-03          6.328-03            1.237+00

           MG++              3.572-01          1.079-01            3.022-01
           MGOH+             4.403-05          3.620-05            8.223-01
           MGSO3             2.955-03          3.657-03            1.237+00
           MGSO4             1.160-01          1.435-01            1.237+00

           OH-               7.888-07          6.487-07            8.223-01
           CL-               6.502-01          3.751-01            5.768-01
           SO3--             2.279-04          2.649-05            1.162-01
           SO4--             7.072-02          5.329-03            7.537-02
          COMPONENT          MOLALITY       ACTIVITY PRODUCT  RELATIVE SATURATION




           CA(OH)2(S)        0.000             1.794-15            5.274-12
           CASO3(S)          0.000             1.822-07            1.778+00
           CASO4(S)          0.000             2.181-05            9.818-01
           MG(OH)2(S)        0.000             4.538-14            4.762-03
           MGSO3(S)          0.000             2.862-05            4.041-02

           PSO2 = 3.13406-10  ATM.

                        MOLECULAR WATER = 1.00500+00 KGS.

                      IONIC STRENGTH = 1.21750+00        RES. E.N. =  -4.153-02
```

RUN NO. E*-11

DATE 2/11/76

ANALYTICAL RESULTS

Species	Standards (% Deviation)	INITIAL Liquid (mmole/l)	INITIAL Solid (mmole/g)	FINAL Liquor (mmole/l)	FINAL Solids (mmole/g)
Ca^{+2}	-.1	18	7.24	23.2	7.21
Mg^{+2}	0	487	.04	479	.05
Na^{+1}	-.8	--	.02	--	.05
Cl^{-1}	.3	636	--	660	--
CO_3^{-2}	--	--	--	--	--
Ts^{-2}	1.0	187	7.02	192	6.96
SO_3^{-2}	--	--	6.43	3.44	6.26
SO_4^{-2}	1.0	187	1.07	188	.92

OPERATING DATA

Time (hr)	pH	Temp. (°C)	SO_3^{-2} (mmole/l)	Solids (wt%)	Solids (g)
0					2.010
288	7.13	48.7	3.55		1.522

COMPUTER RESULTS

Ionic Strength	Residual Electroneutrality	Relative Saturation $CaSO_3\cdot\frac{1}{2}H_2O$	Relative Saturation $CaSO_4\cdot 2H_2O$	Relative Saturation $CaSO_4\cdot\frac{1}{2}H_2O$	Mole Fraction SO_3^{-2}	Mole Fraction SO_4^{-2}
1.22	-.038	1.72	.94	.41	.87	.13

COMMENTS

RUN NO. E-11

DATE 2/11/76

REACTOR MATERIAL BALANCE CALCULATIONS

Run # E*-11 Date 2/11/76

INLET		Liquid	Solid	Σ
Flow Rate		570 ml	2.011 g	
Ca^{+2}	(mmole)	10.3	14.6	24.9
Mg^{+2}	(mmole)	278.	.08	278.
Na_2^{+2}	(mmole)	----	.04	.04
Cl^{-1}	(mmole)	362.	----	362.
T_s	(mmole)	107.	14.1	121.
SO_3^{-2}	(mmole)	----	12.9	12.9
SO_4^{-2}	(mmole)	107.	2.2	109.

OUTLET		Liquid	Solid	Σ
Flow Rate		570 ml	1.52 g	
Ca^{+2}	(mmole)	13.22	11.0	24.2
Mg^{+2}	(mmole)	273.	----	273.
Na_2^{+2}	(mmole)	----	0.08	0.08
Cl^{-1}	(mmole)	376.	----	376.
T_s	(mmole)	109.	10.6	120.
SO_3^{-2}	(mmole)	2.02	9.52	11.5
SO_4^{-2}	(mmole)	107.	1.4	108.

SOLIDS MATERIAL BALANCE

Run # E#-11 Date 2/11/76

	g/mmole	mmole/gram	g/gram
Ca^{+2}	.040	7.21	.288
Mg^{+2}	.024	.05	.001
Na_2^{+2}	.046	.05	.002
Cl^{-1}	.035	--	--
CO_3^{-2}	.060	--	--
SO_3^{-2}	.080	6.26	.501
SO_4^{-2}	.096	.92	.088
$\frac{1}{2}H_2O$	.009	7.18	.065
			Σ .945

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EQUILIBRIUM RUN 11

```
03 MAR 76    14:15:10.133                                  TEMPERATURE    48.700 DEG. C.
                                 INPUT SPECIES (MOLES)

              H2O  = 5.55062+01                 HCL  = 6.60000-01
              CAO  = 2.32000-02                 CO2  = 0.00000
              MGO  = 4.79000-01                 N2O3 = 0.00000
              NA2O = 0.00000                    N2O5 = 0.00000
                                                SO2  = 3.55000-03
                                                SO3  = 1.80000-01

     PH =  7.1300

     SUPERSATURATION ALLOWED

                     AQUEOUS SOLUTION EQUILIBRIA

     COMPONENT          MOLALITY           ACTIVITY      ACTIVITY COEFFICIENT

      H+               9.194-08           7.411-08          1.198+00
      H2O                                                   9.8[illegible]-01
      H2SO3            3.597-14           4.454-14          1.238+00
      HSO3-            7.953-05           4.765-05          5.992-01
      HSO4-            9.227-08           7.594-08          8.231-01

      CA++             1.787-02           4.208-03          2.355-01
      CAOH+            9.492-08           7.812-08          8.231-01
      CASO3            3.159-04           3.911-04          1.238+00
      CASO4            4.877-03           6.039-03          1.238+00

      MG++             3.508-01           1.060-01          3.023-01
      MGOH+            4.563-05           3.759-05          8.231-01
      MGSO3            2.917-03           3.612-03          1.238+00
      MGSO4            1.134-01           1.404-01          1.238+00

      OH-              8.154-07           6.711-07          8.231-01
      CL-              9.581-01           3.744-01          3.768-01
      SO3--            2.154-04           2.779-05          1.289-01
      SO4--            6.862-02           5.163-03          7.525-02
     COMPONENT          MOLALITY       ACTIVITY PRODUCT  RELATIVE SATURATION




      CA(OH)2(S)       0.000              1.896-15          5.548-10
      CASO3(S)         0.000              1.152-07          1.717+00
      CASO4(S)         0.000              2.287-05          9.380-01
      MG(OH)2(S)       0.000              4.899-14          5.134-03
      MGSO3(S)         0.000              2.894-06          4.820-02

      PSO2 = 8.45529-12  ATM.

                MOLECULAR WATER = 1.00544+00 KGS.

             IONIC STRENGTH = 1.22114+00        RES. E.N. =  -3.844-02
```

RUN NO. E*-12

DATE 2/11/76

ANALYTICAL RESULTS

		INITIAL		FINAL	
Species	Standards (% Deviation)	Liquid (mmole/l)	Solid (mmole/g)	Liquor (mmole/l)	Solids (mmole/g)
Ca^{+2}	-.1	18	7.24	23.1	7.11
Mg^{+2}	0	487	.04	482	.04
Na^{+1}	-.8		.02	--	.05
Cl^{-1}	.3	636		655	--
CO$_3{}^{-2}$	--			--	--
Ts^{-2}	1.0	187	7.02	198	698
SO$_3{}^{-2}$	--		6.43	3.59	6.32
SO$_4{}^{-2}$	1.0	187	1.07	194	.94

OPERATING DATA

Time (hr)	pH	Temp. (°C)	SO$_3{}^{-2}$ (mmole/l)	Solids (wt%)	Solids (g)
0		50			2.000
288	6.95	48	3.59		1.510

COMPUTER RESULTS

		Relative Saturation			Mole Fraction	
Ionic Strength	Residual Electroneutrality	$CaSO_3 \cdot \frac{1}{2}H_2O$	$CaSO_4 \cdot 2H_2O$	$CaSO_4 \cdot \frac{1}{2}H_2O$	SO$_3{}^{-2}$	SO$_4{}^{-2}$
1.22	-.040	1.70	.96	.41	.87	.13

COMMENTS

RUN NO. E*-12
DATE 2/11/76

REACTOR MATERIAL BALANCE CALCULATIONS

Run # E*-12 Date 2/11/76

INLET		Liquid	Solid	Σ
Flow Rate		570 ml	2.000 g	
Ca^{+2}	(mmole)	10.3	14.5	24.8
Mg^{+2}	(mmole)	278.	.08	278.
Na_2^{+2}	(mmole)	----	.04	.04
Cl^{-1}	(mmole)	362.	----	362.
T_s	(mmole)	107.	14.0	121.
SO_3^{-2}	(mmole)	----	12.9	12.9
SO_4^{-2}	(mmole)	107.	2.1	109.

OUTLET		Liquid	Solid	Σ
Flow Rate		570 ml	1.51 g	
Ca^{+2}	(mmole)	13.2	10.7	23.9
Mg^{+2}	(mmole)	275.	----	275.
Na_2^{+2}	(mmole)	----	.08	.08
Cl^{-1}	(mmole)	373.	----	373.
T_s	(mmole)	113.	10.53	124.
SO_3^{-2}	(mmole)	205.	9.54	11.6
SO_4^{-2}	(mmole)	111.	1.42	112.

SOLIDS MATERIAL BALANCE

Run # E#-12 Date 2/11/76

	g/mmole	mmole/gram	g/gram
Ca^{+2}	.040	7.11	.284
Mg^{+2}	.024	.04	.001
Na_2^{+2}	.046	.05	.002
Cl^{-1}	.035	--	--
CO_3^{-2}	.060	--	--
SO_3^{-2}	.080	6.32	.506
SO_4^{-2}	.096	.94	.090
$\frac{1}{2}H_2O$	.009	7.26	.065
		Σ	.949

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EQUILIBRIUM RUN 12

```
03 MAR 75    14115119.431                              TEMPERATURE    48.000 DEG. C.
                                 INPUT SPECIES (MOLES)

                 H2O  = 5.55062+01                 HCL  = 6.55000-01
                 CAO  = 2.31000-02                 CO2  = 0.00000
                 MGO  = 4.82000-01                 N2O3 = 0.00000
                 NA2O = 0.00000                    N2O5 = 0.00000
                                                   SO2  = 3.59000-03
                                                   SO3  = 1.94200-01

      PH =  6.9501

      SUPERSATURATION ALLOWED

                        AQUEOUS SOLUTION EQUILIBRIA

     COMPONENT          MOLALITY             ACTIVITY    ACTIVITY COEFFICIENT

      H+                9.385-08             1.122-07          1.195+00
      H2O                                                      9.840-01
      H2SO3             7.982-12             9.883-12          1.238+00
      HSO3-             1.194-04             7.159-05          5.996-01
      HSO4-             1.413-07             1.163-07          8.231-01

      CA++              1.772-02             4.175-03          2.359-01
      CAOH+             5.936-08             4.886-08          8.231-01
      CASO3             3.110-04             3.850-04          1.238+00
      CASO4             4.953-03             6.133-03          1.238+00

      MG++              3.501-01             1.057-01          3.027-01
      MGOH+             2.874-05             2.365-05          8.231-01
      MGSO3             2.922-03             3.618-03          1.238+00
      MGSO4             1.172-01             1.451-01          1.238+00

      OH-               5.164-07             4.251-07          8.231-01
      CL-               6.512-01             3.758-01          5.772-01
      SO3--             2.164-04             2.796-05          1.292-01
      SO4--             7.074-02             5.340-03          7.549-02
     COMPONENT          MOLALITY         ACTIVITY PRODUCT  RELATIVE SATURATION




      CA(OH)2(S)        0.000                7.544-18          2.174-10
      CASO3(S)          0.000                1.156-07          1.699+00
      CASO4(S)          0.000                2.142-05          9.579-01
      MG(OH)2(S)        0.000                1.904-14          2.041-03
      MGSO3(S)          0.000                2.802-06          4.755-02
     PSO2 = 1.76900-09  ATM.

                  MOLECULAR WATER = 1.00590+00 KGS.

                 IONIC STRENGTH = 1.22127+00        RES. E.N. =  -3.966-02
```

APPENDIX F

INFRARED SPECTRA OF PRECIPITATED SOLIDS FROM LABORATORY AND PILOT PLANT STUDIES

Prepared by:

Benjamin F. Jones
Frank B. Meserole

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INFRARED SPECTRA

1.0 INTRODUCTION

Infrared spectroscopy has been applied to both the qualitative identification and quantitative determination of the calcium sulfite-sulfate solid solution. Infrared spectral analysis has been performed on selected solids precipitated in the equilibrium runs and the kinetic runs. Pure phase calcium sulfite hemihydrate, calcium sulfate dihydrate, calcium carbonate, and dolomite have been analyzed by infrared spectroscopy for reference purposes. In addition, actual pilot plant scrubber samples from the EPA scrubber at Research Triangle Park, North Carolina, and the Radian/Joy/PP&L scrubber at Sunbury, Pennsylvania have been analyzed by IR spectroscopy.

2.0 QUALITATIVE APPLICATION OF INFRARED SPECTRAL ANALYSIS

Infrared spectroscopy was successfully used to confirm the presence of sulfate in the calcium sulfite solids. The infrared absorption due to the sulfate ion showed that the incorporation occurred by the substitution of a sulfate ion for a sulfite ion in the crystal lattice. The vibrational spectral structure of any pure phase sulfate compound such as $CaSO_4 \cdot 2H_2O$ in the 1100 cm^{-1} region is characteristically broad with little or no resolution of the three component bands. In case of the matrix isolation as occurs in a solid solution, the peak positions shift and a greater degree of resolution can be observed. Solids identified as containing sulfate by chemical analysis and spectroscopically appeared to be solid solutions were analyzed by X-ray diffraction and differential scanning calorimetry. Both techniques failed to show the presence of a pure phase sulfate compound, specifically indicating that no gypsum was present.

For comparative purposes, the IR spectra of pure calcium sulfite hemihydrate and calcium sulfate dihydrate are shown in Figure 2-1. The absorption structures of interest are the major sulfite band at approximately 980 cm^{-1} and the sulfate band near 1130 cm^{-1}. The structure in the 3200-3600 cm^{-1} and 1600-1700 cm^{-1} ranges are a result of the waters of hydration of the two solids. The absorption bands in the 600-700 cm^{-1} region are due to the sulfite and sulfate ions but are not as distinctive as the major bands.

The infrared spectra of two solid samples from the experimental precipitaiton studies are shown in Figure 2-2. The upper spectrum is that of the solids precipitated from a solution supersaturated in calcium sulfite hemihydrate and subsaturated

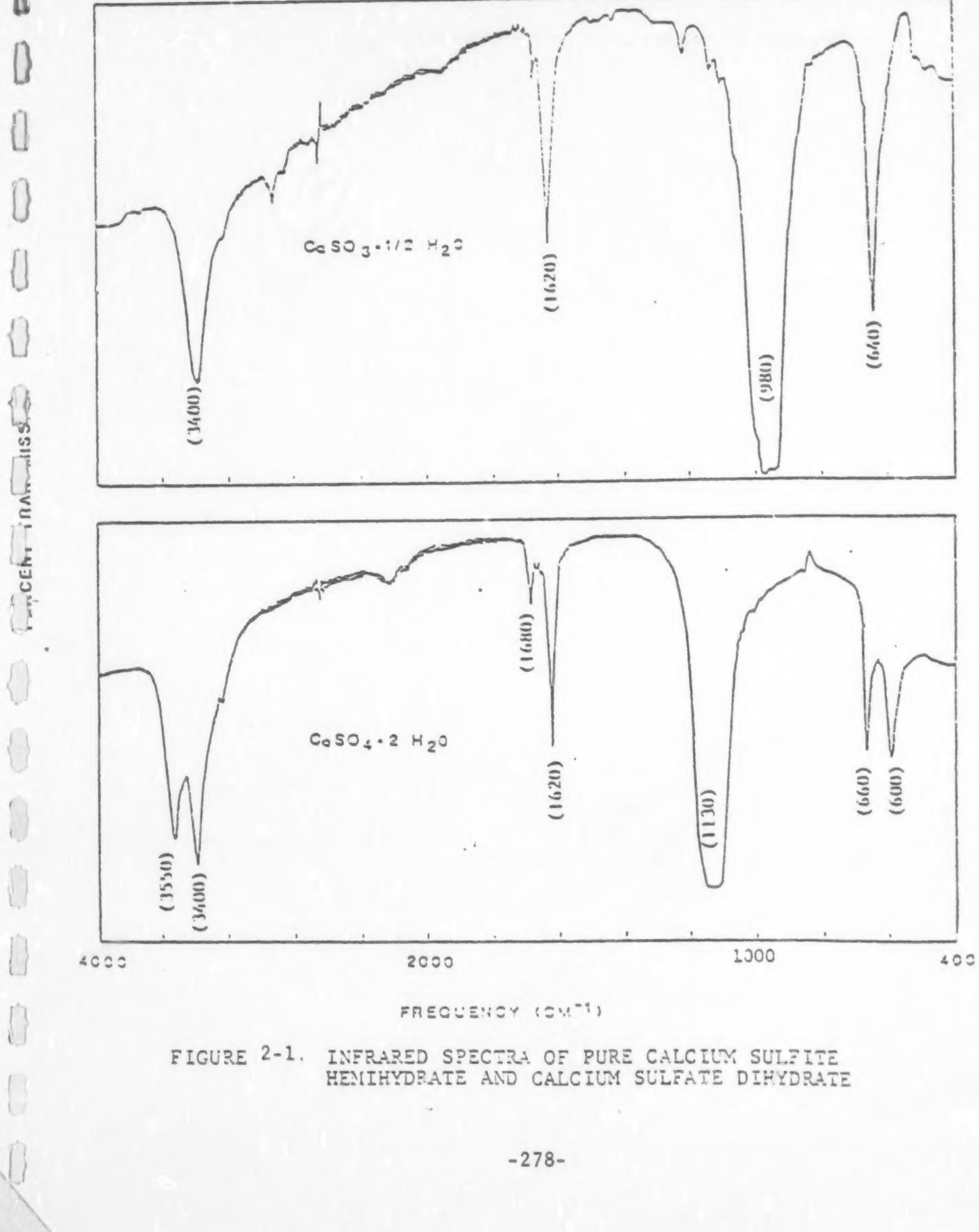


FIGURE 2-1. INFRARED SPECTRA OF PURE CALCIUM SULFITE HEMIHYDRATE AND CALCIUM SULFATE DIHYDRATE

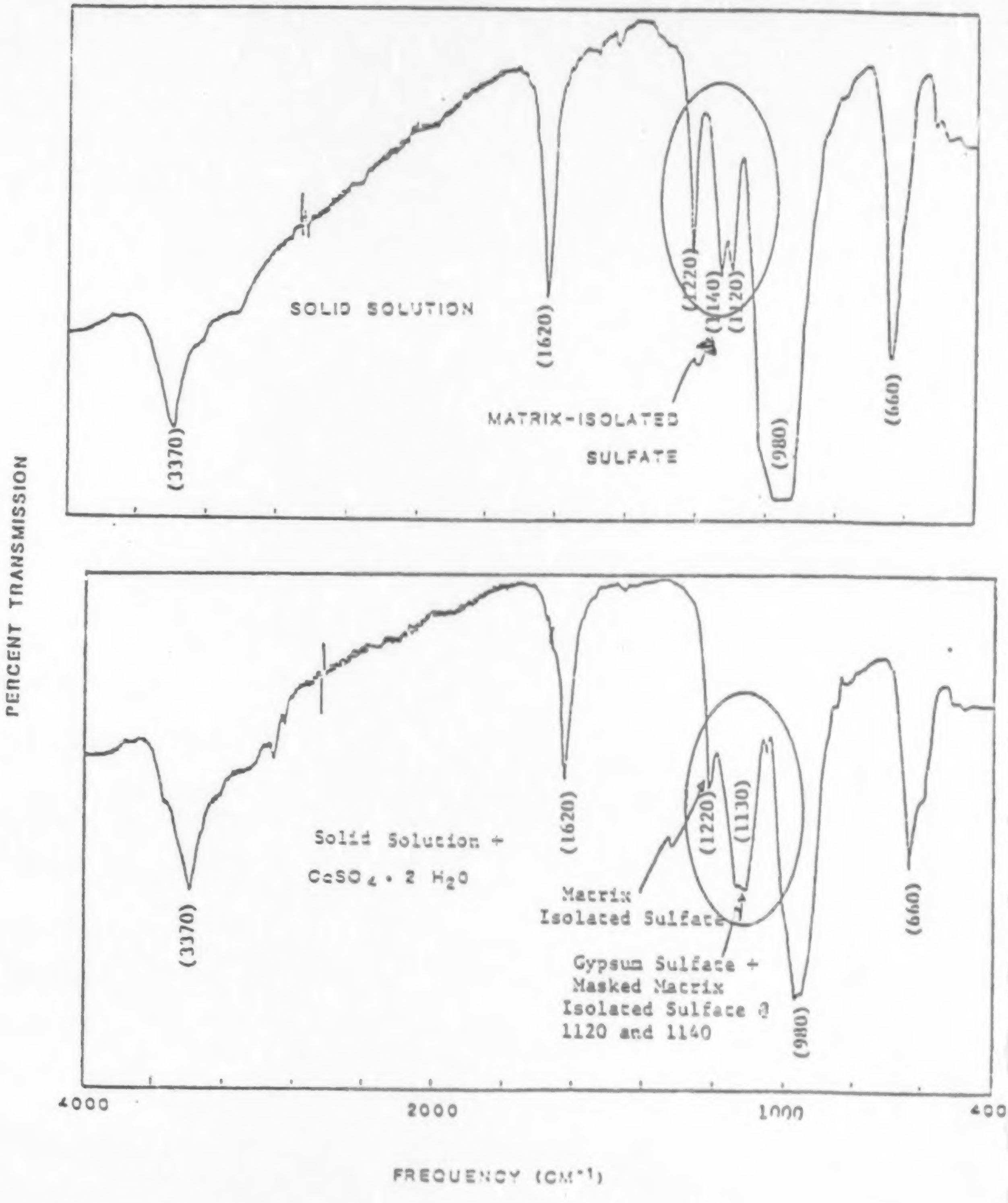


FIGURE 2-2. INFRARED SPECTRA OF REACTOR PRODUCTS

with respect to calcium sulfate dihydrate. The band structure encircled is indicative of the IR absorption due to matrix isolated sulfate ion.

The lower spectrum is that of the solids precipitated from a solution supersaturated in both calcium sulfite hemihydrate and calcium sulfate dihydrate. In this case, the structure in the sulfate sorption region shows the presence of sulfate as both pure phase gypsum and in solid solution with calcium sulfite hemihydrate. The presence of gypsum was verified using X-ray diffractions and DSC analyses.

The following is a simplified explanation of the spectral differences of the sulfate ion in a pure phase crystal or in solid solution with another compound. In the first place, the absorption of electromagnetic radiation in this spectral region results from a coupling of the incident radiation with the vibrational modes of the sulfate ion. Quantum theory predicts three different frequencies. In the case of a pure phase sulfate compound, the frequency range of these vibrations is broadened due to the interaction or coupling of the vibrational modes of neighboring sulfate ions. The matrix isolation of sulfate ions in the solid solution effectively dilutes the sulfate ions as compared to a pure phase system and thus reduces the coupling effect. The frequency shifts and narrowing of the bands are a direct result of the decoupling of the intermolecular interaction of the sulfate ion vibrational modes.

Thus, the combination of these instrumental techniques has been used to verify the existence of the coprecipitation of sulfate with calcium sulfite as a solid solution. In addition, it was demonstrated that the IR spectroscopy can be used to distinguish between the sulfate in a solid solution or as gypsum.

3.0 QUANTITATIVE APPLICATION OF INFRARED SPECTRAL ANALYSIS

Infrared analysis was also used to quantitatively measure the sulfate concentration in the solid solution. The technique was initially calibrated by comparison of the ratio of the sulfate absorbance at 1220 cm^{-1} to that of the water band at 1620 cm^{-1} with sulfate concentrations determined by the specific chemical method. In the absence of gypsum, the following equation is used to calculate mole fraction of sulfate, $x_{SO_4^{-2}}$ in a solid from the infrared sorption measurements:

$$x_{SO_4^{-2}} = \frac{C_{SO_4^{-2}}}{C_{T_s}} = \frac{C_{SO_4^{-2}}}{2C_{H_2O}} = k\frac{A_{SO_4^{-2}}}{A_{H_2O}} = k\,\frac{(\log \frac{T_b}{T_m})\ SO_4^{-2}}{(\log \frac{T_b}{T_m})\ H_2O}$$

where,

$C_{SO_4^{-2}}$ = the concentration of sulfate in the solids (mole SO_4^{-2}/g sample),

C_{T_s} = the concentration of sulfate plus sulfite in the solids (mole $SO_4^{-2} + SO_3^{-2}$/g sample),

C_{H_2O} = concentration of the hydration water in the solids (mole H_2O/g sample),

k = a constant,

$A_{SO_4^{-2}}$ = the IR absorbance at 1220 cm^{-1},

A_{H_2O} = the IR absorbance at 1620 cm^{-1}, and

T_b/T_m = the ratio of the percent transmission values at the base line and transmission minimum for the appropriate band.

The correlation of the spectral and chemical results are shown graphically in Figure 2-3. The accuracy limits at the 95% confidence level is ±.02 in the sulfate mole fraction based on a linear least square fit to the data.

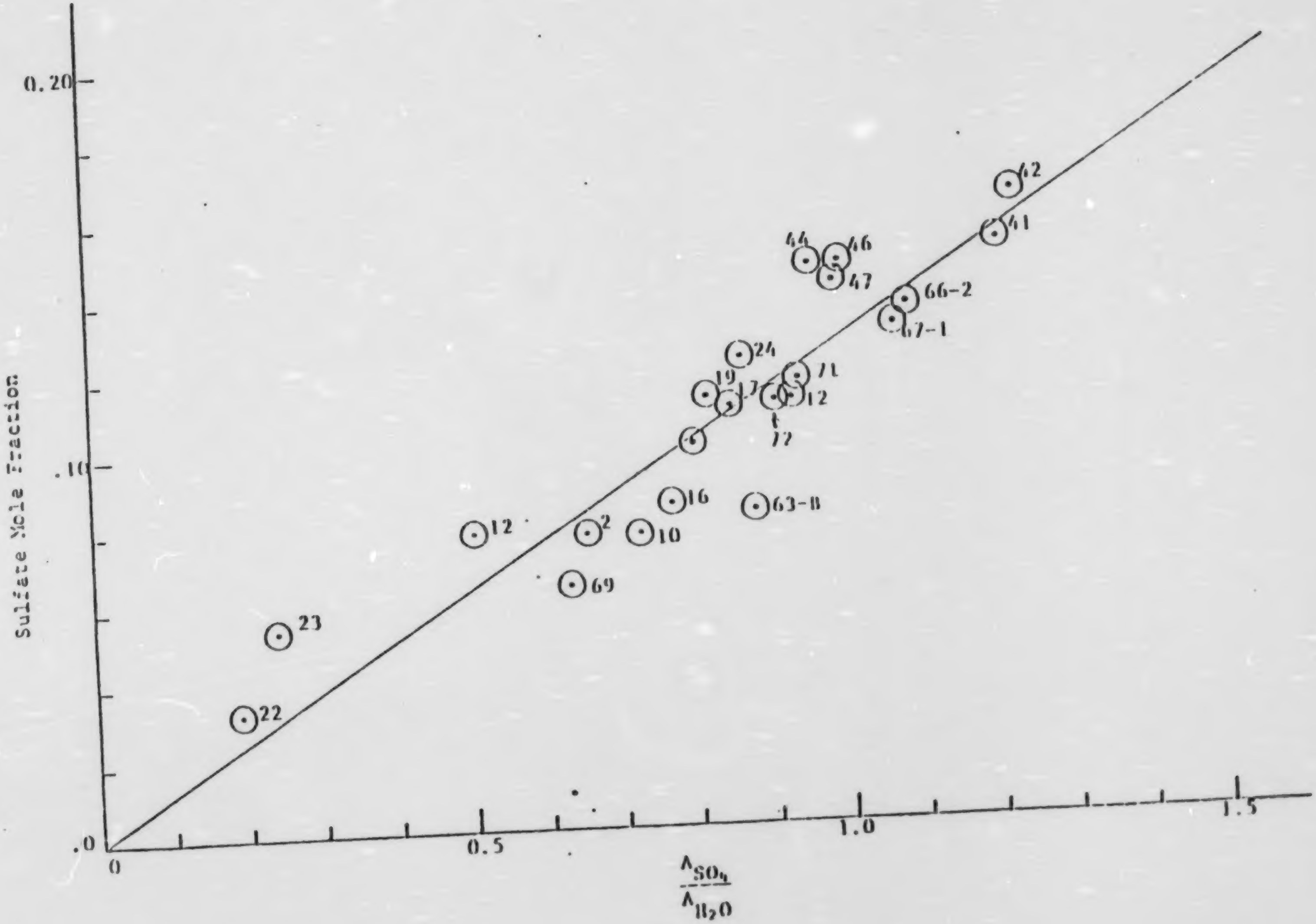


FIGURE 2-3. RESULTS OF INFRARED QUANTITATIVE CORRELATION OF SULFATE MOLE FRACTION WITH THE RATIO OF THE ABSORBANCE OF THE SULFATE BAND (1220 cm^{-1}) WITH THE H$_2$O BAND (1620 cm^{-1})

INFRARED SPECTRA

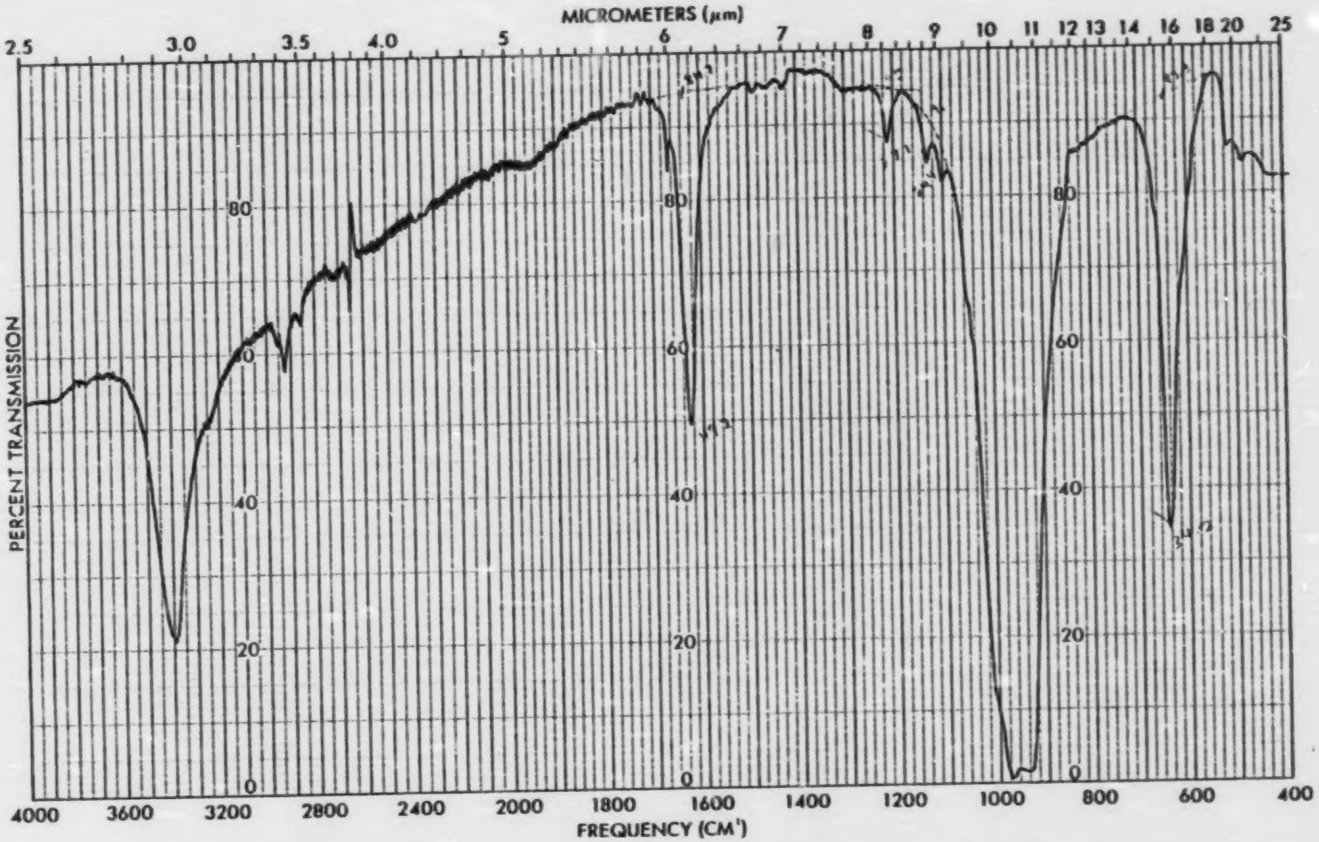


FIGURE F-1. INFRARED SPECTRA OF $CaSO_3 \cdot \frac{1}{2}H_2O$

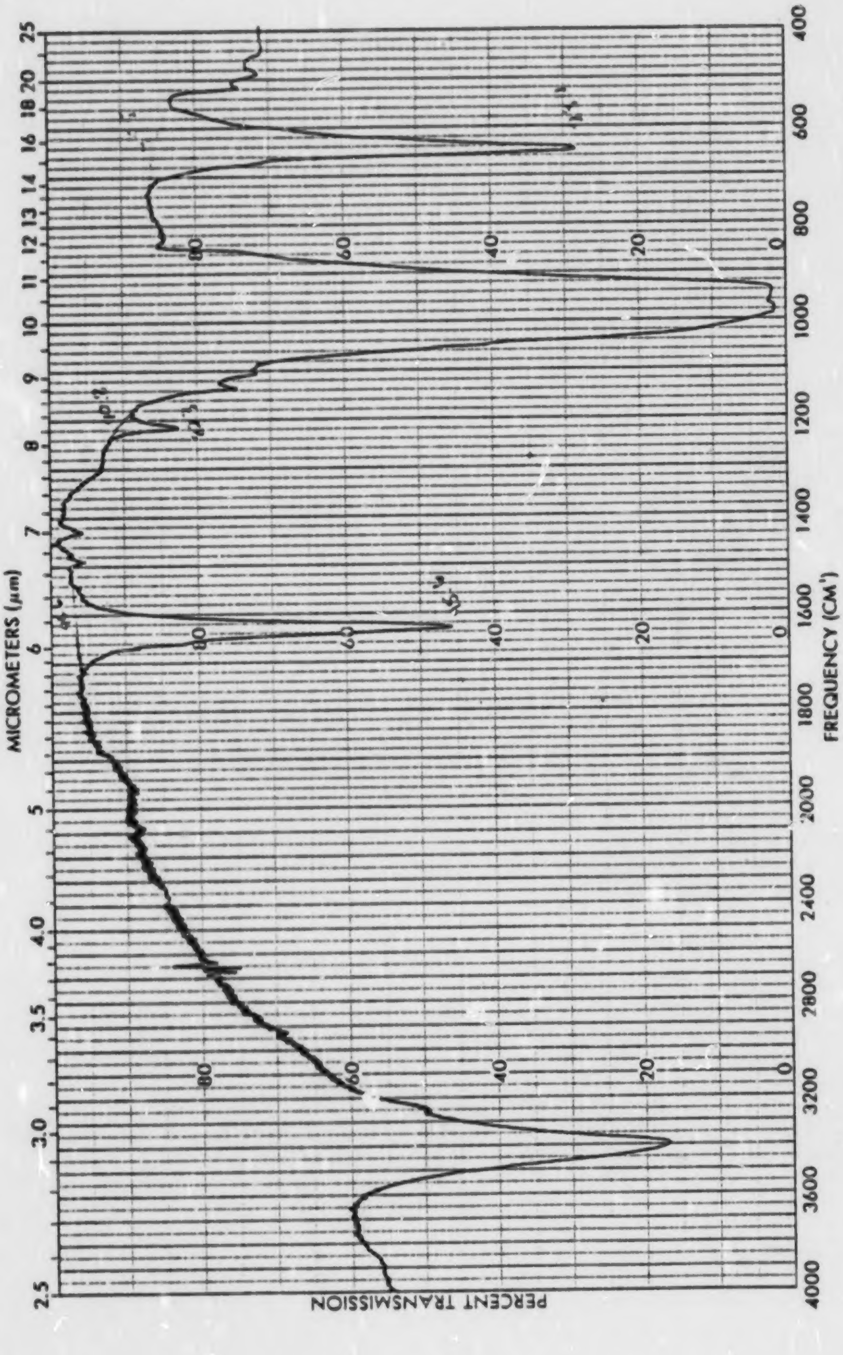


FIGURE F-2. INFRARED SPECTRA OF $CaSO_3 \cdot \frac{1}{2}H_2O$

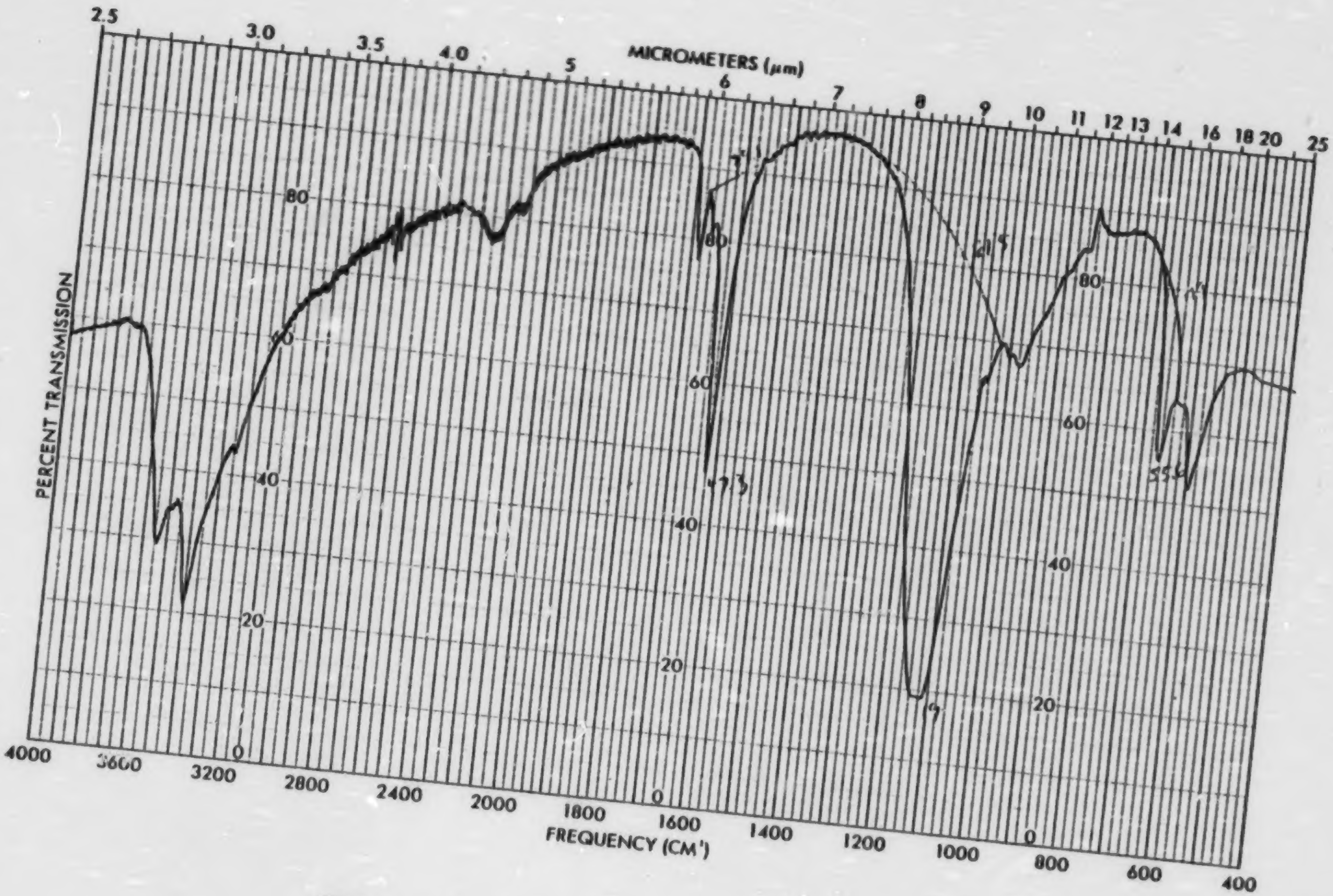


FIGURE F-3. INFRARED SPECTRA OF $CaSO_4 \cdot 2H_2O$

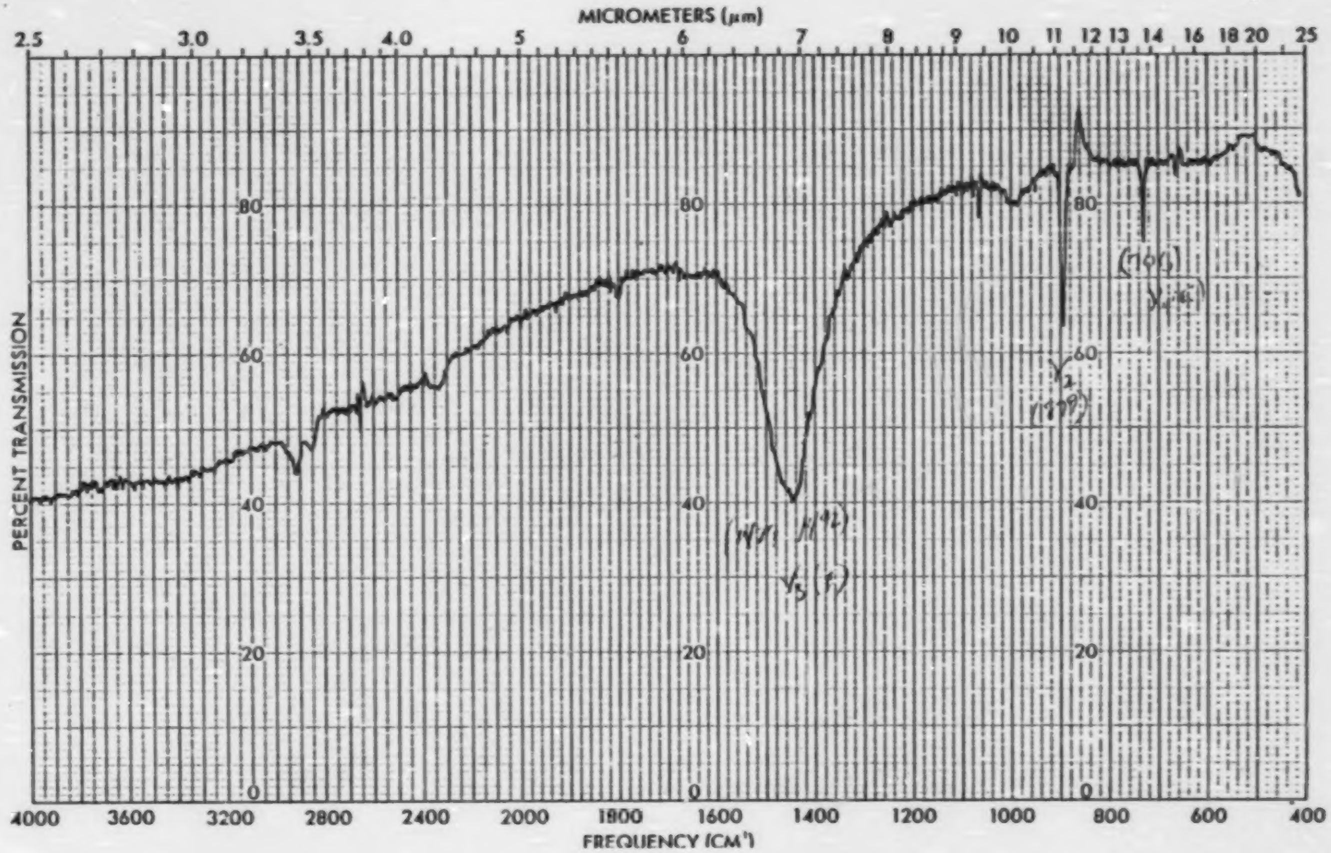


FIGURE F-4.   INFRARED SPECTRA OF $CaCO_3$

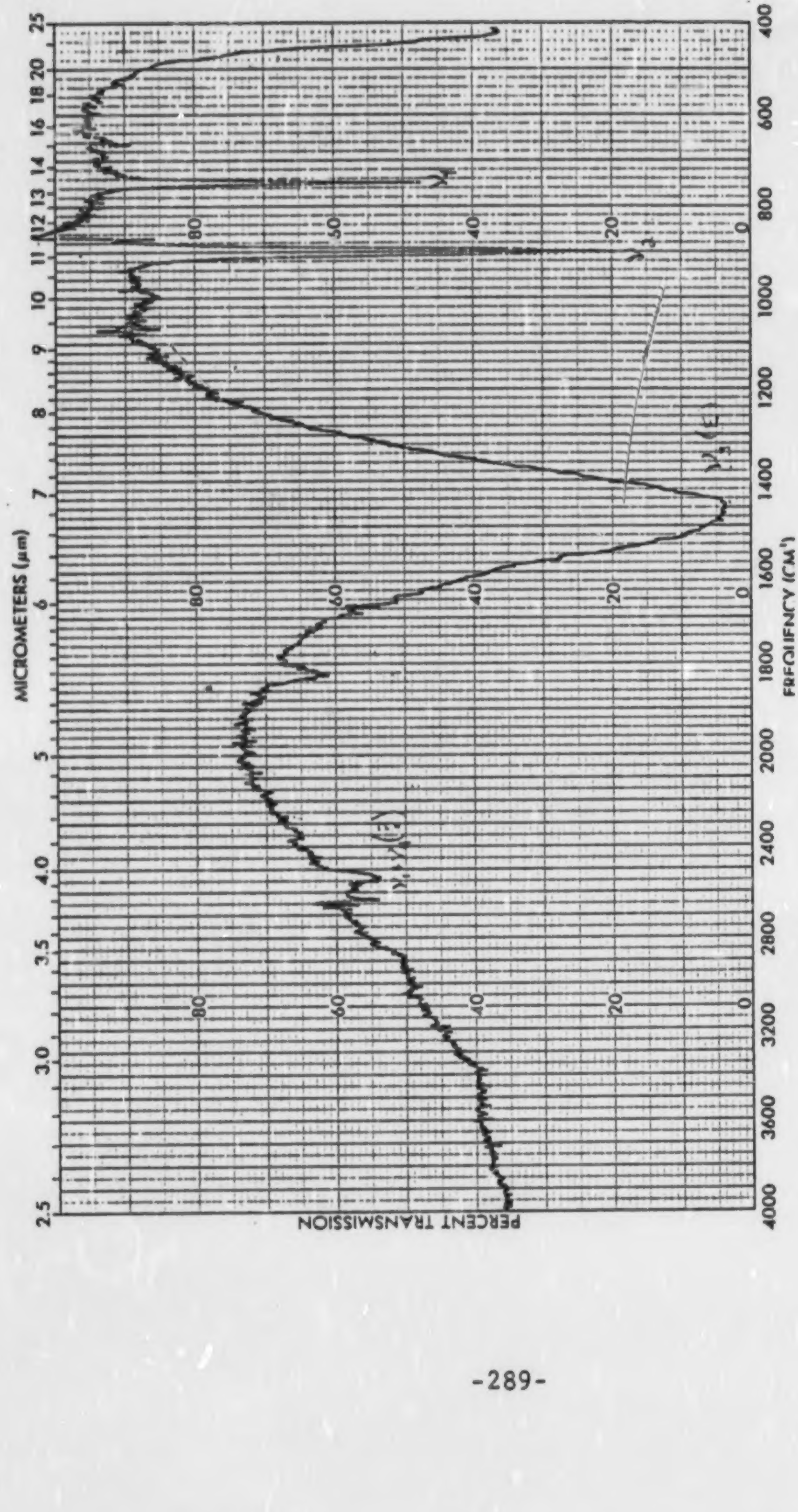


FIGURE F-5. INFRARED SPECTRA OF DOLOMITE

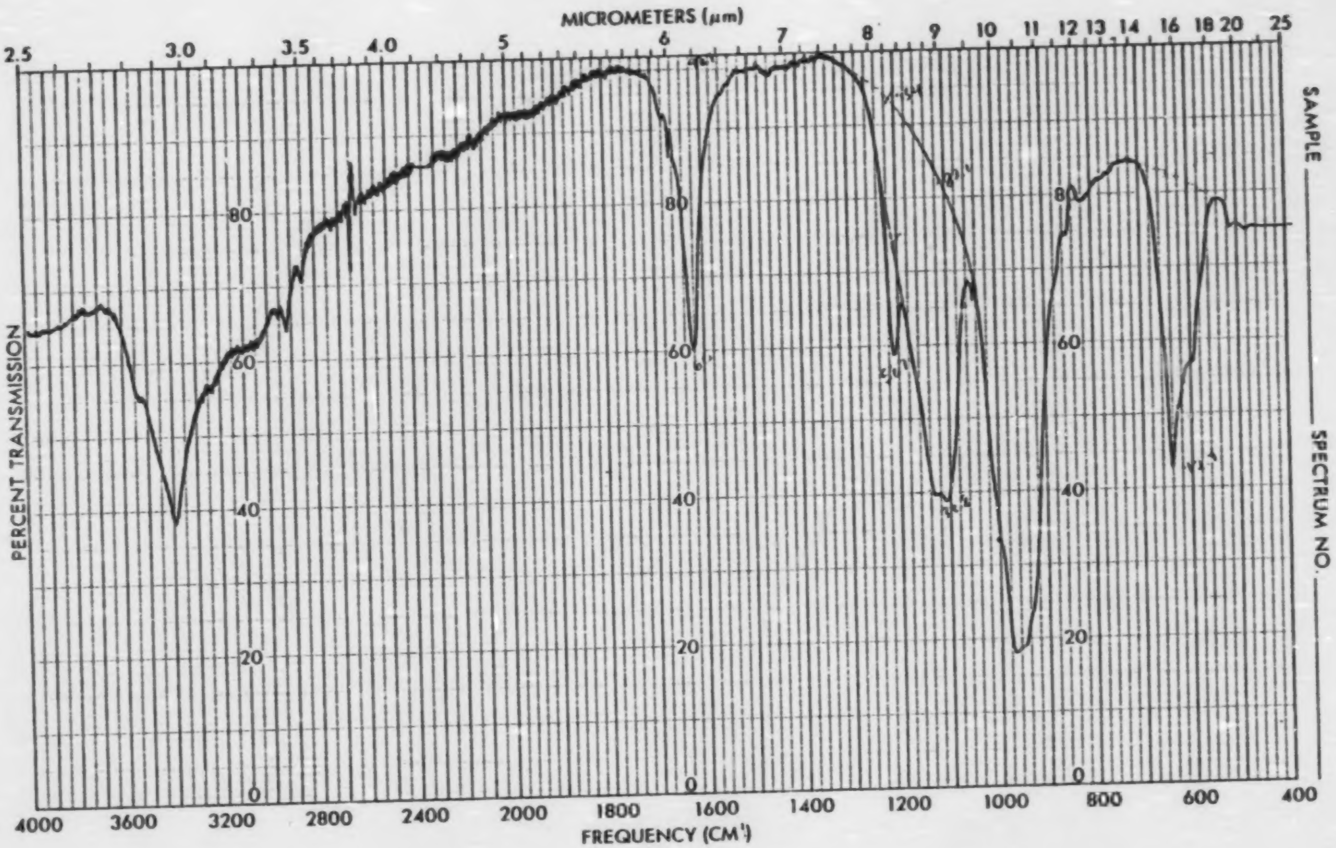


FIGURE F-6. INFRARED SPECTRA OF EQUILIBRIUM RUN 5 PRECIPITATED SOLIDS

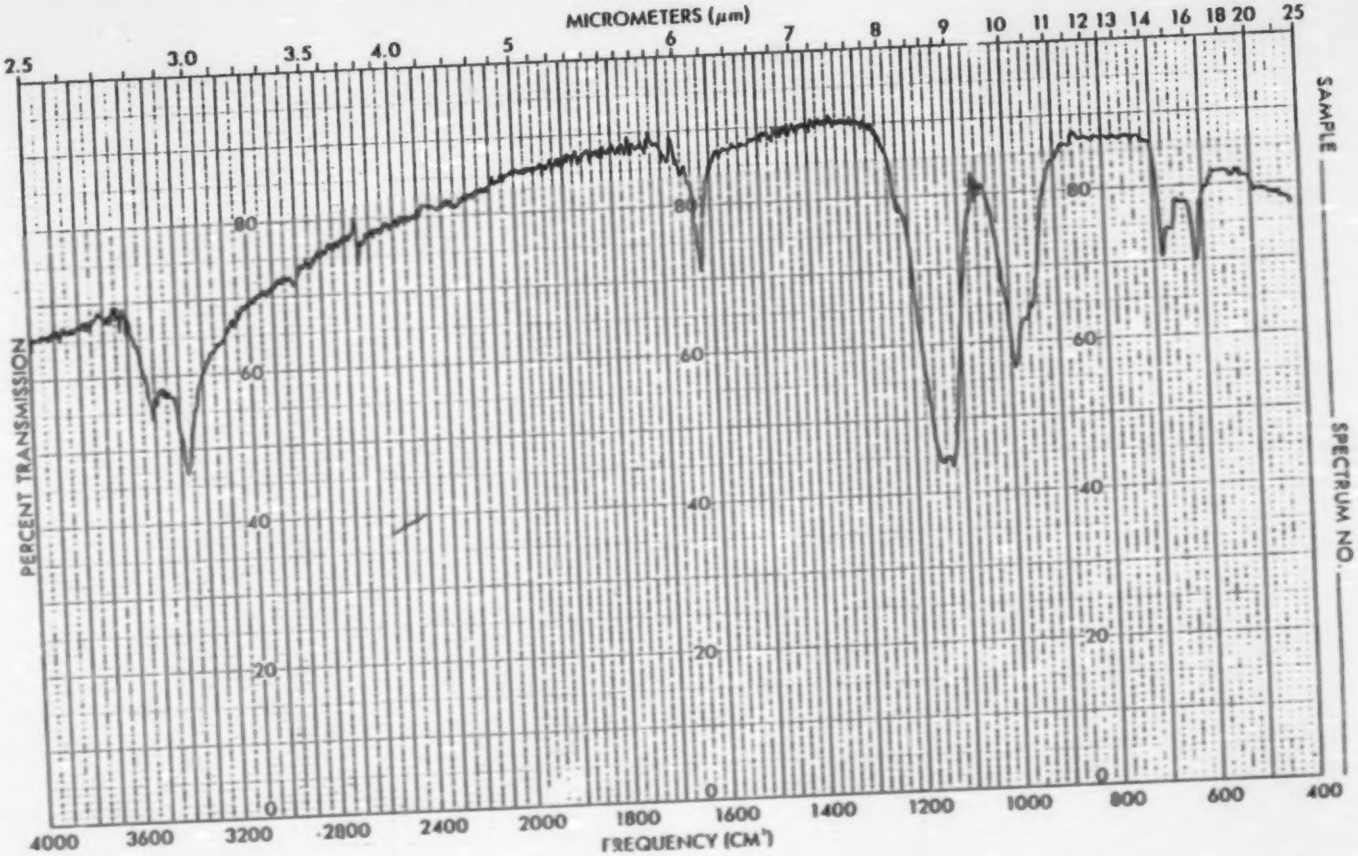


FIGURE F-7. INFRARED SPECTRA OF EQUILIBRIUM RUN 6
PRECIPITATED SOLIDS

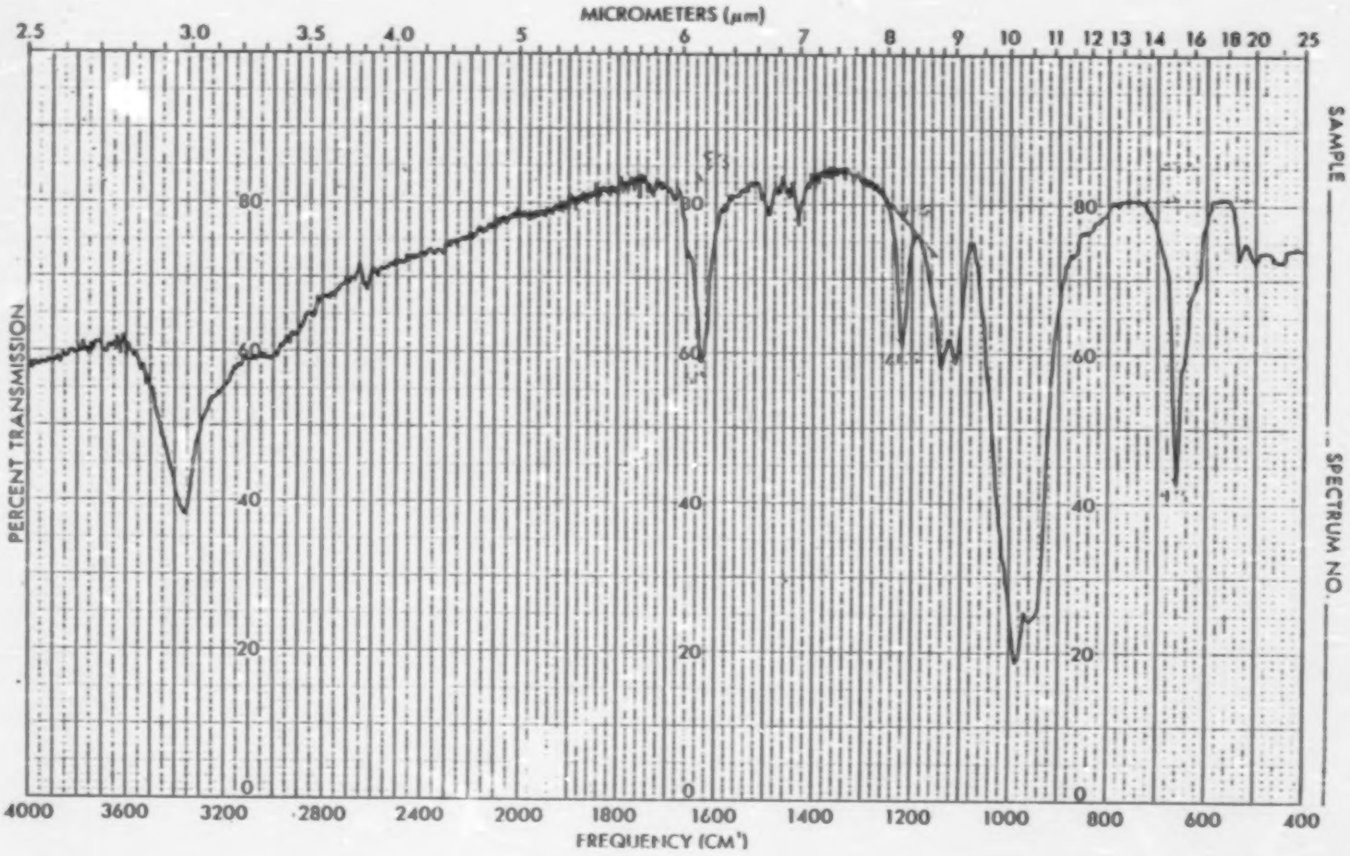


FIGURE F-8. INFRARED SPECTRA OF EQUILIBRIUM RUN 8 PRECIPITATED SOLIDS

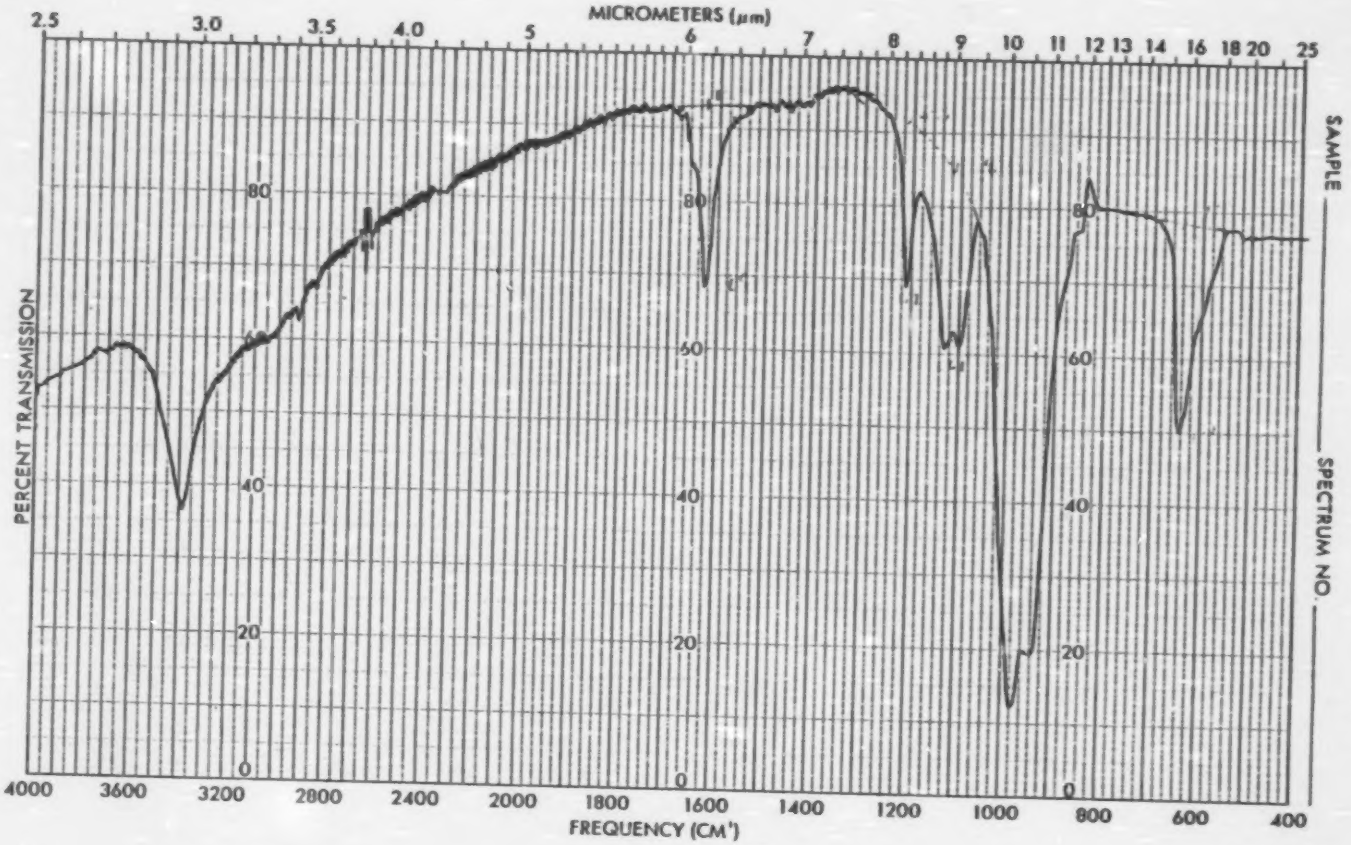


FIGURE F-9. INFRARED SPECTRA OF EQUILIBRIUM RUN 9 PRECIPITATED SOLIDS

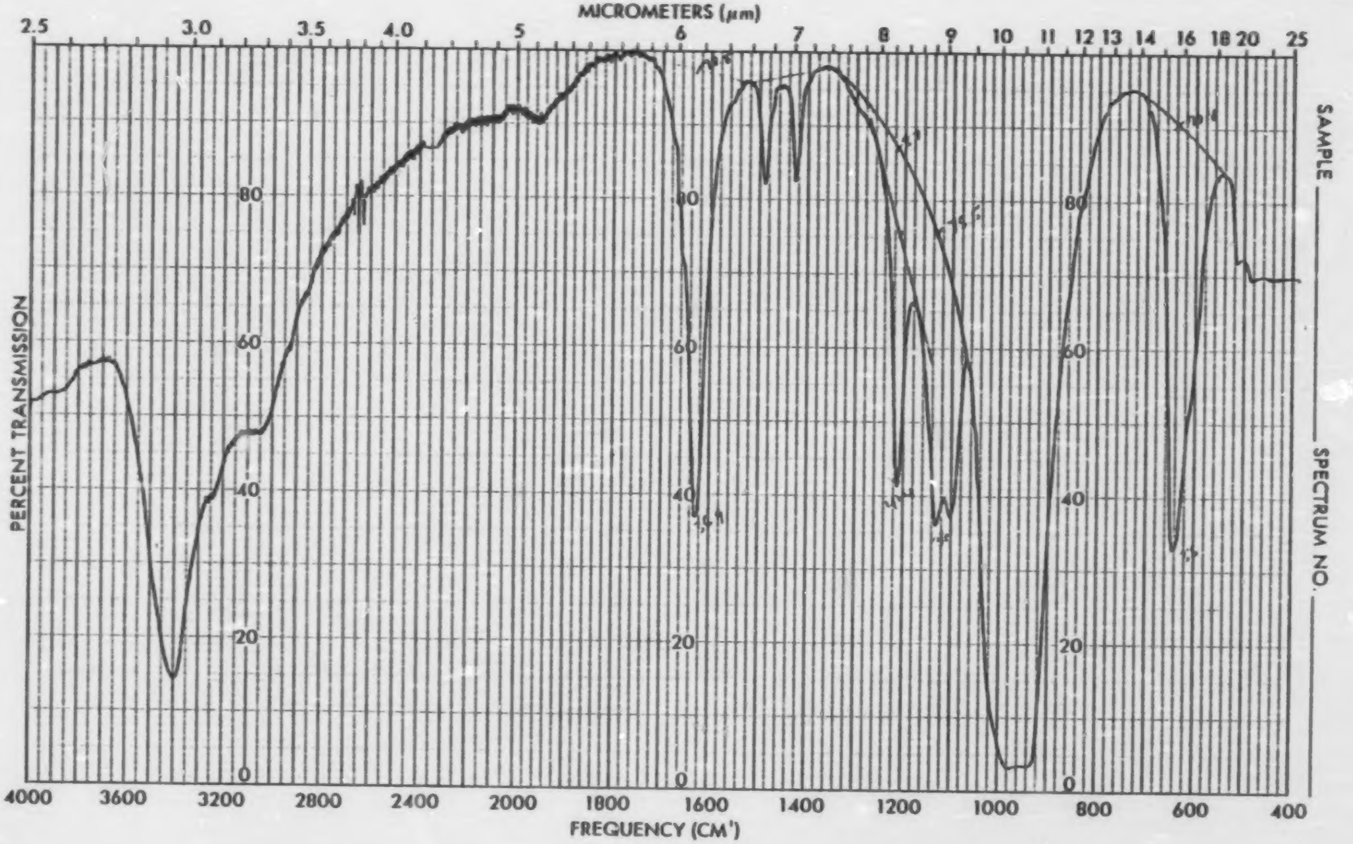


FIGURE F-10. INFRARED SPECTRA OF KINETIC RUN 2 PRECIPITATED SOLIDS

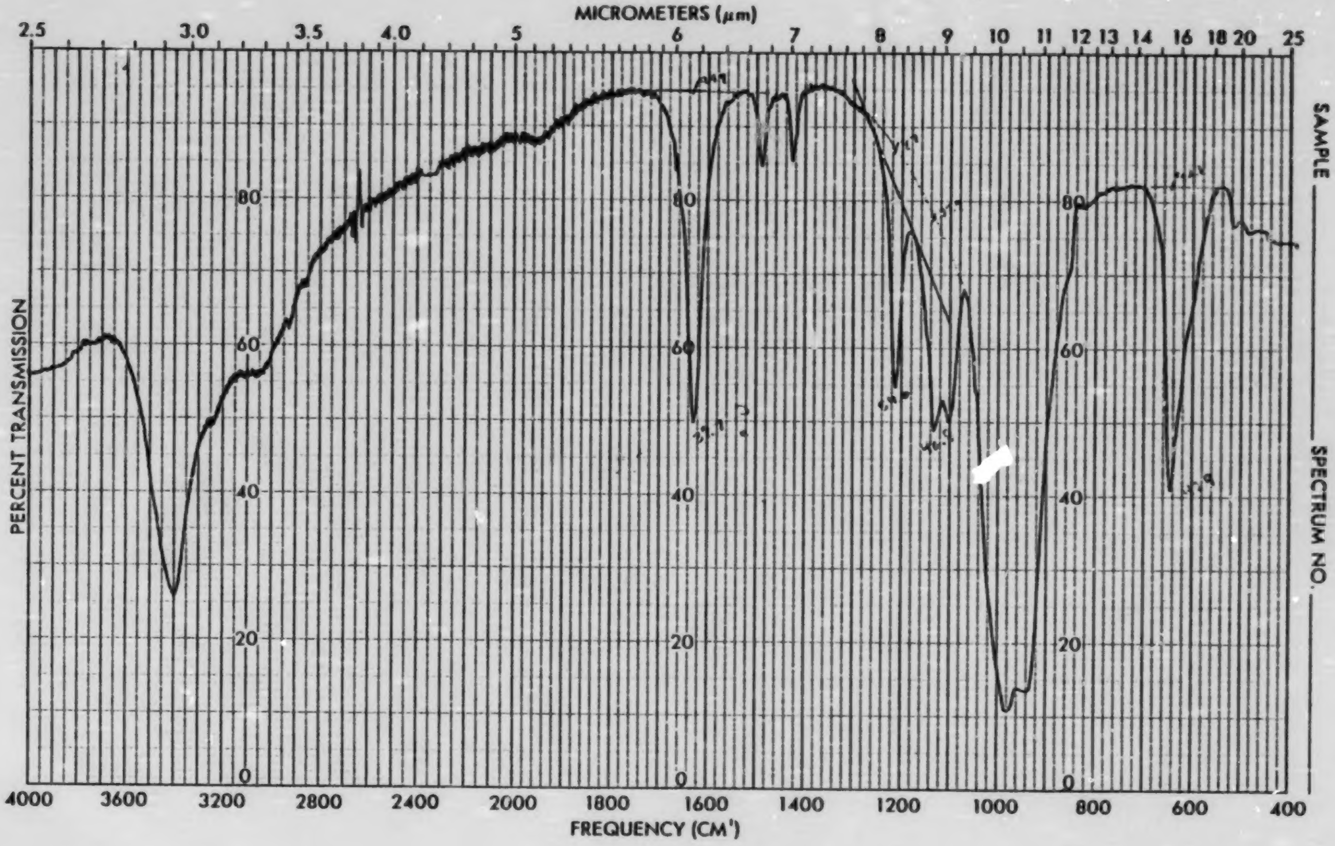


FIGURE F-11. INFRARED SPECTRA OF KINETIC RUN 2 PRECIPITATED SOLIDS

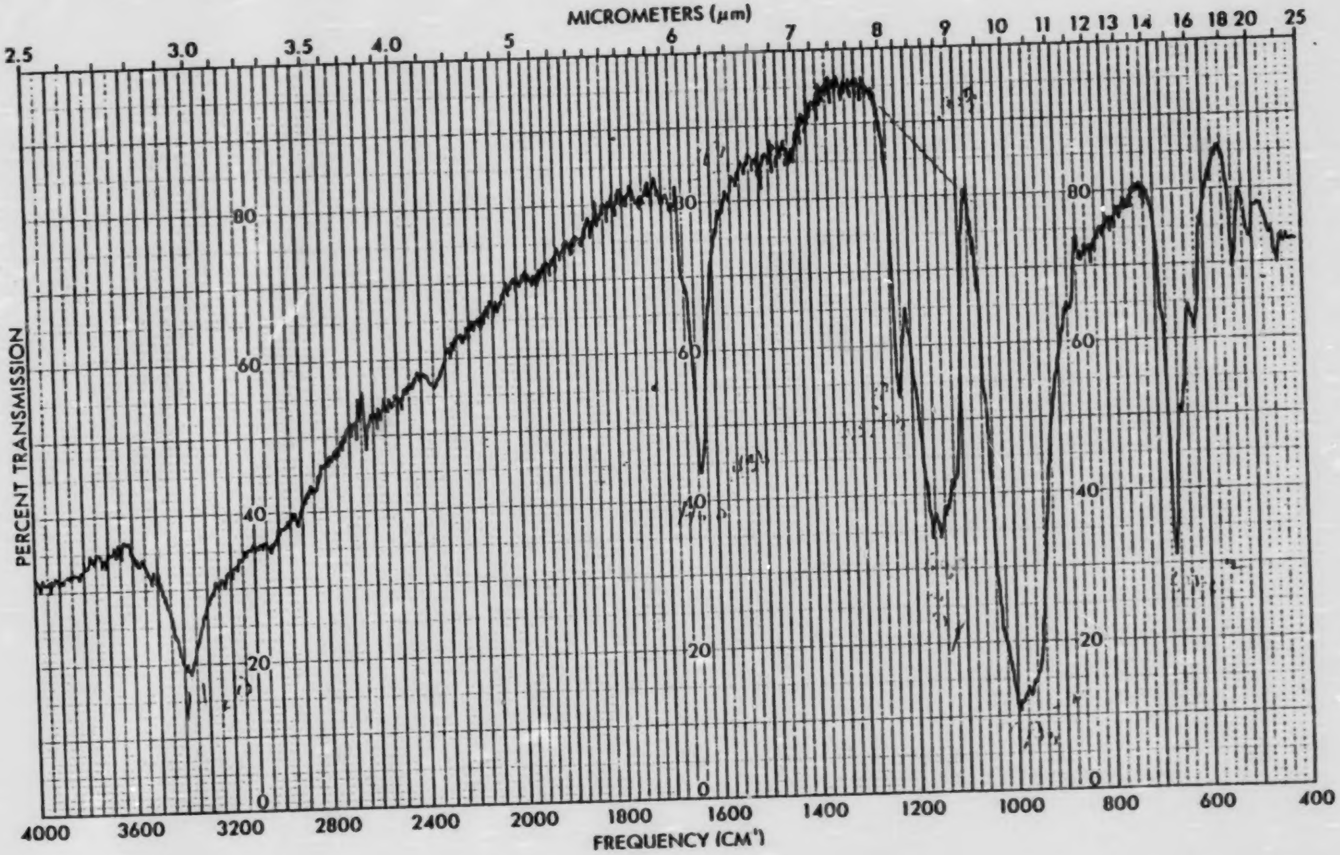


FIGURE F-12. INFRARED SPECTRA OF KINETIC RUN 9 PRECIPITATED SOLIDS

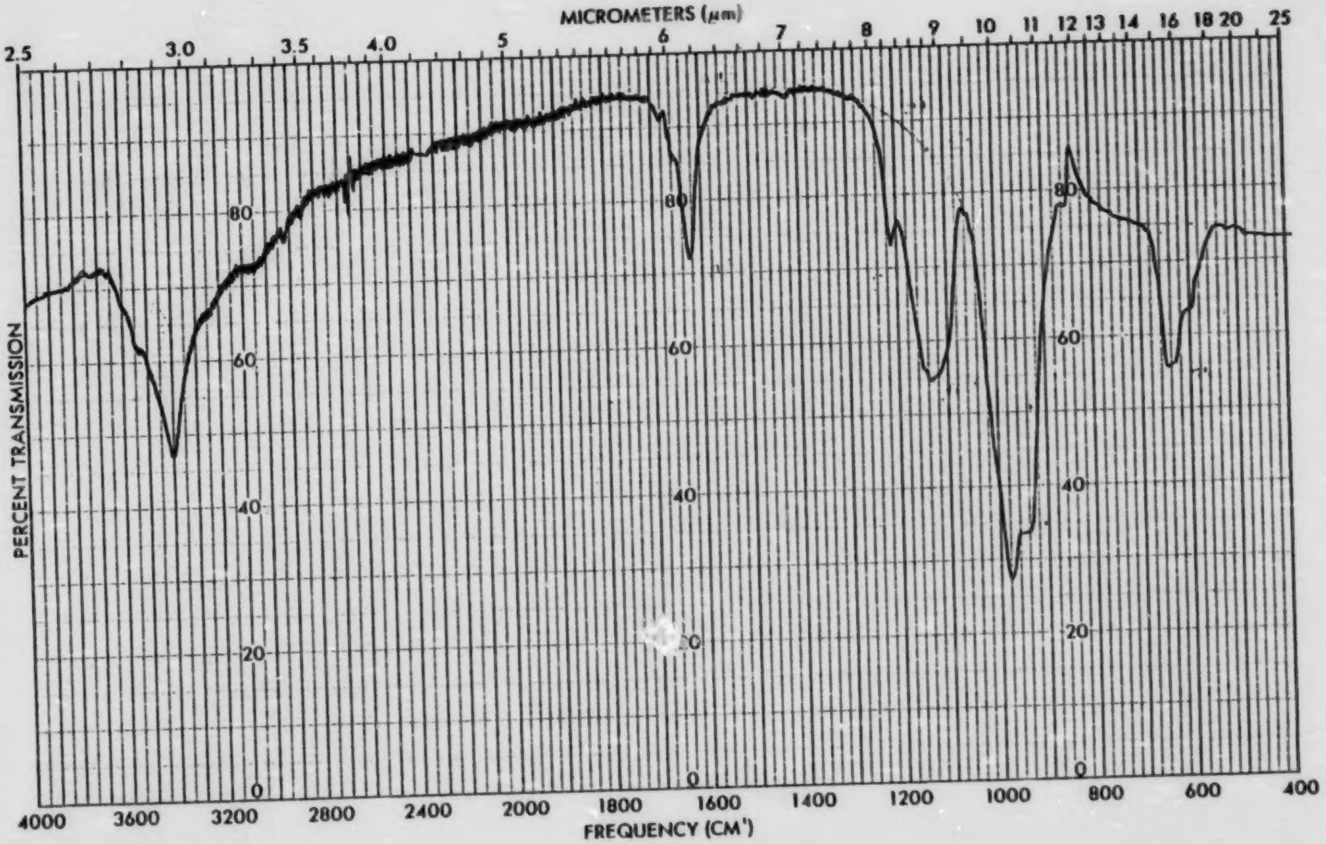


FIGURE F-13. INFRARED SPECTRA OF KINETIC RUN 9
PRECIPITATED SOLIDS

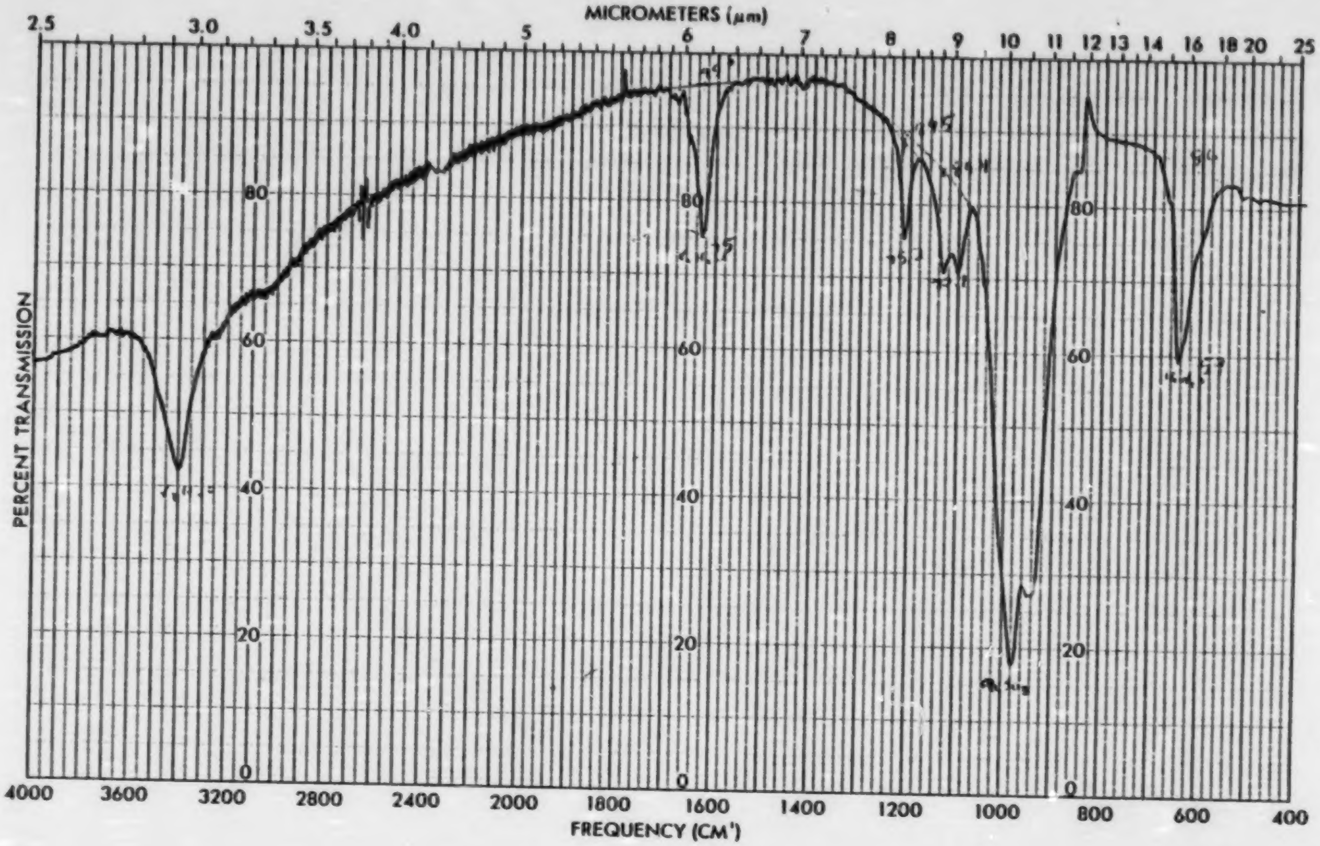


FIGURE F-14. INFRARED SPECTRA OF KINETIC RUN 10 PRECIPITATED SOLIDS

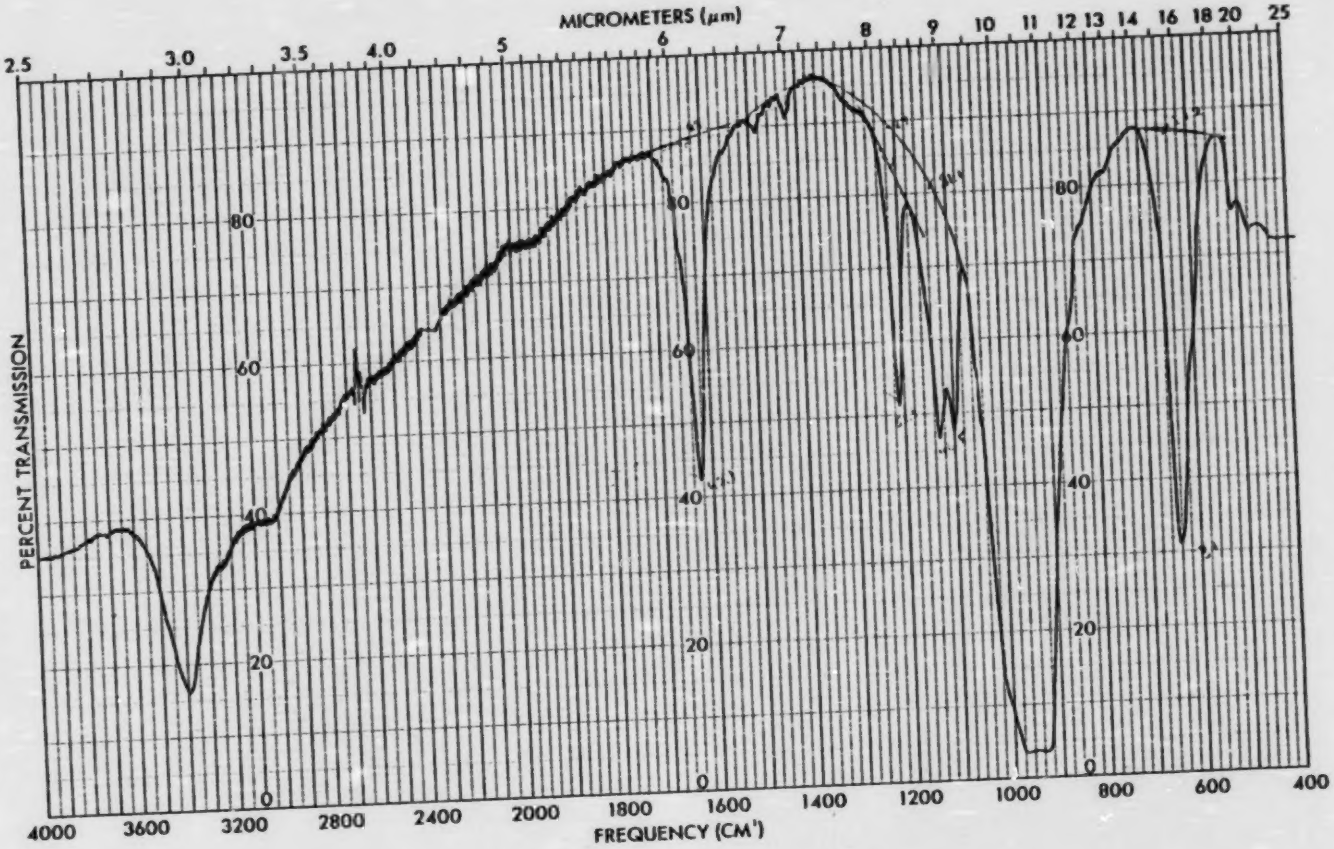


FIGURE F-15. INFRARED SPECTRA OF KINETIC RUN 10
PRECIPITATED SOLIDS

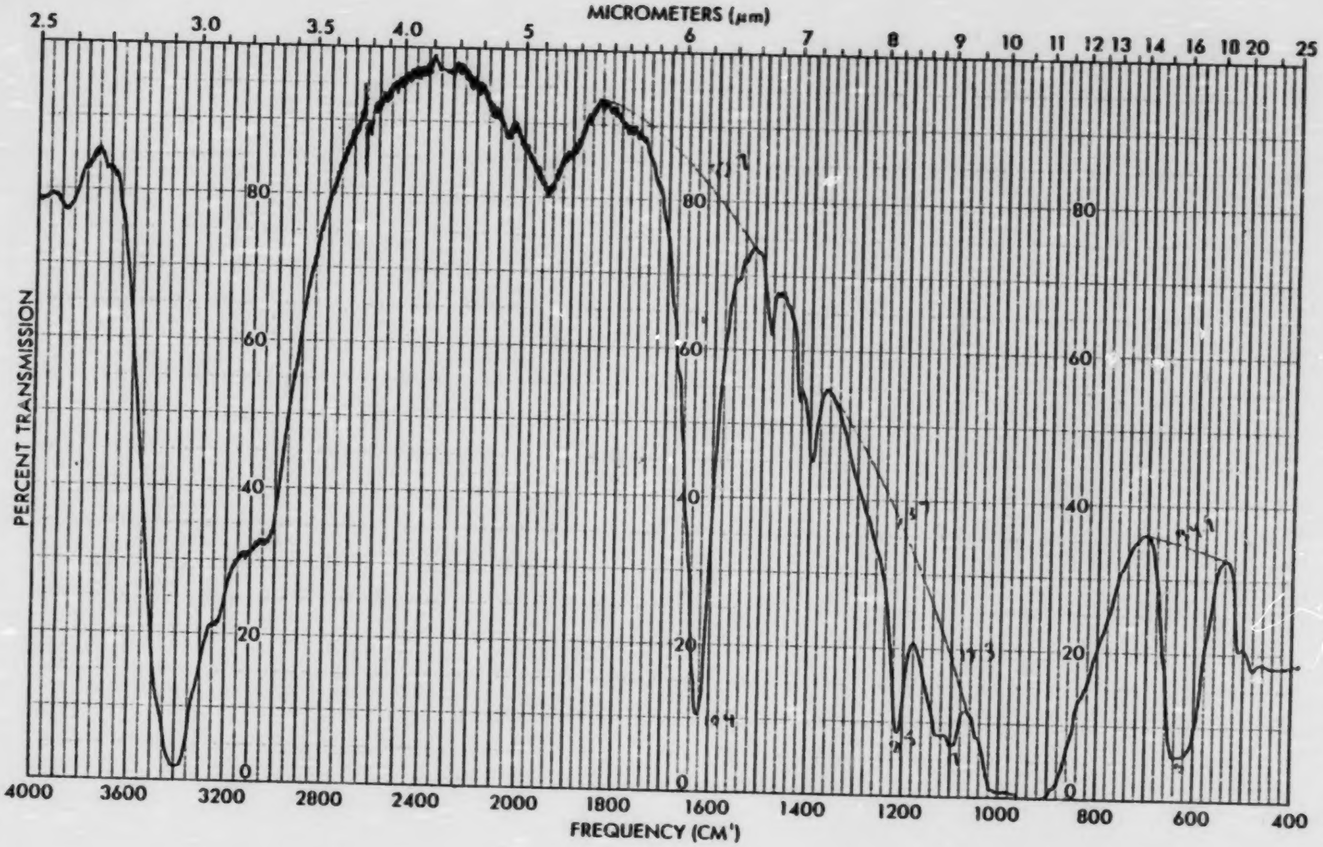


FIGURE F-16. INFRARED SPECTRA OF KINETIC RUN 10 PRECIPITATED SOLIDS

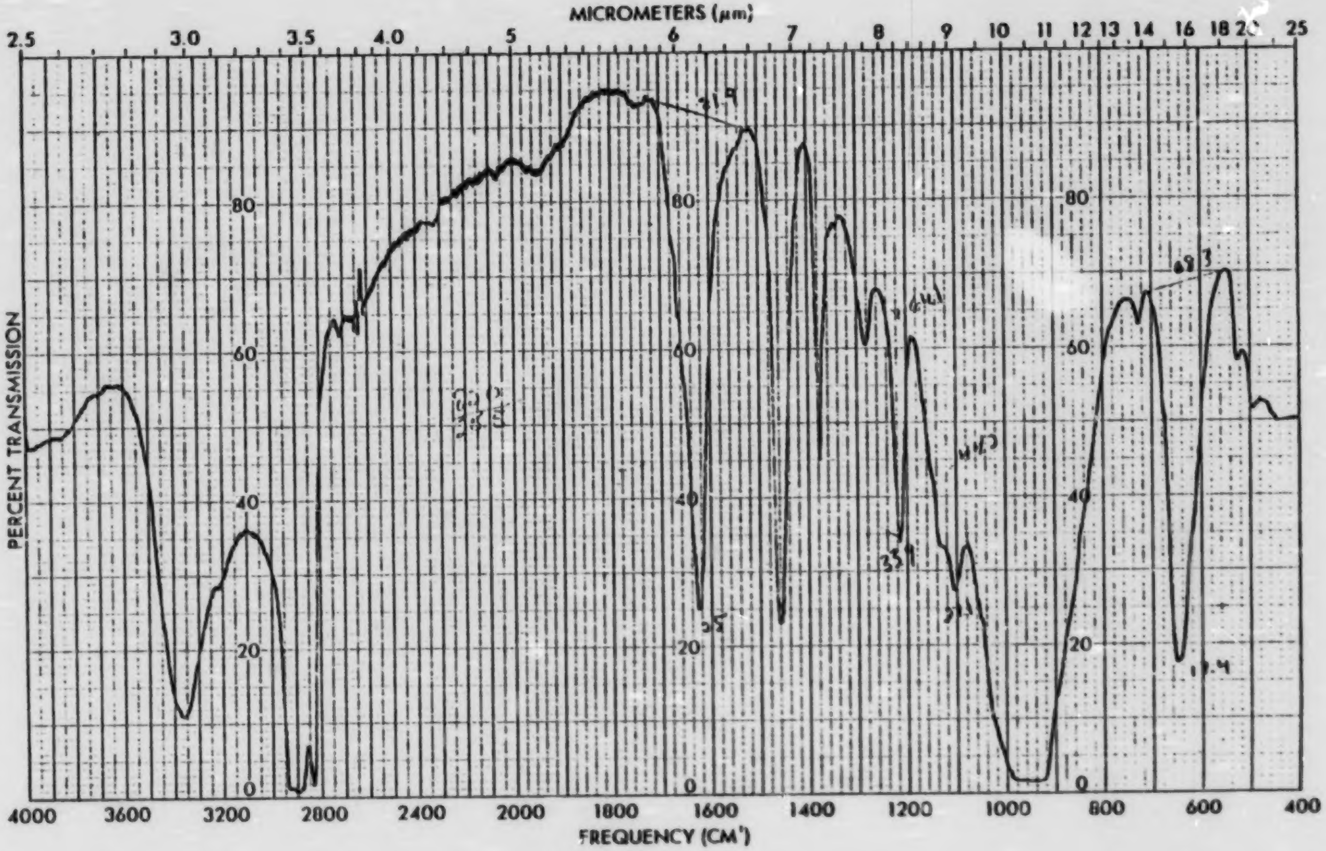


FIGURE F-17. INFRARED SPECTRA OF KINETIC RUN 12
PRECIPITATED SOLIDS

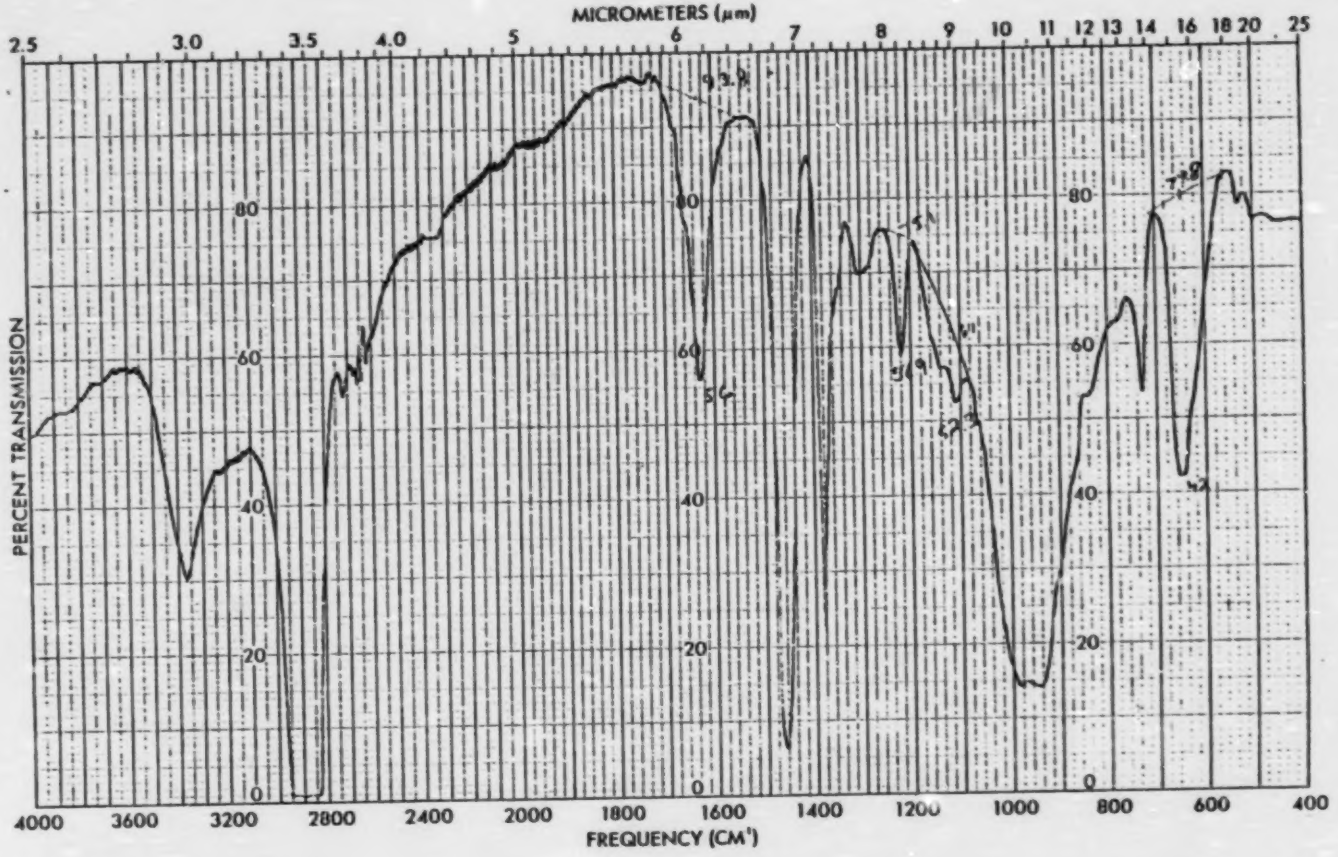


FIGURE F-18. INFRARED SPECTRA OF KINETIC RUN 12 PRECIPITATED SOLIDS

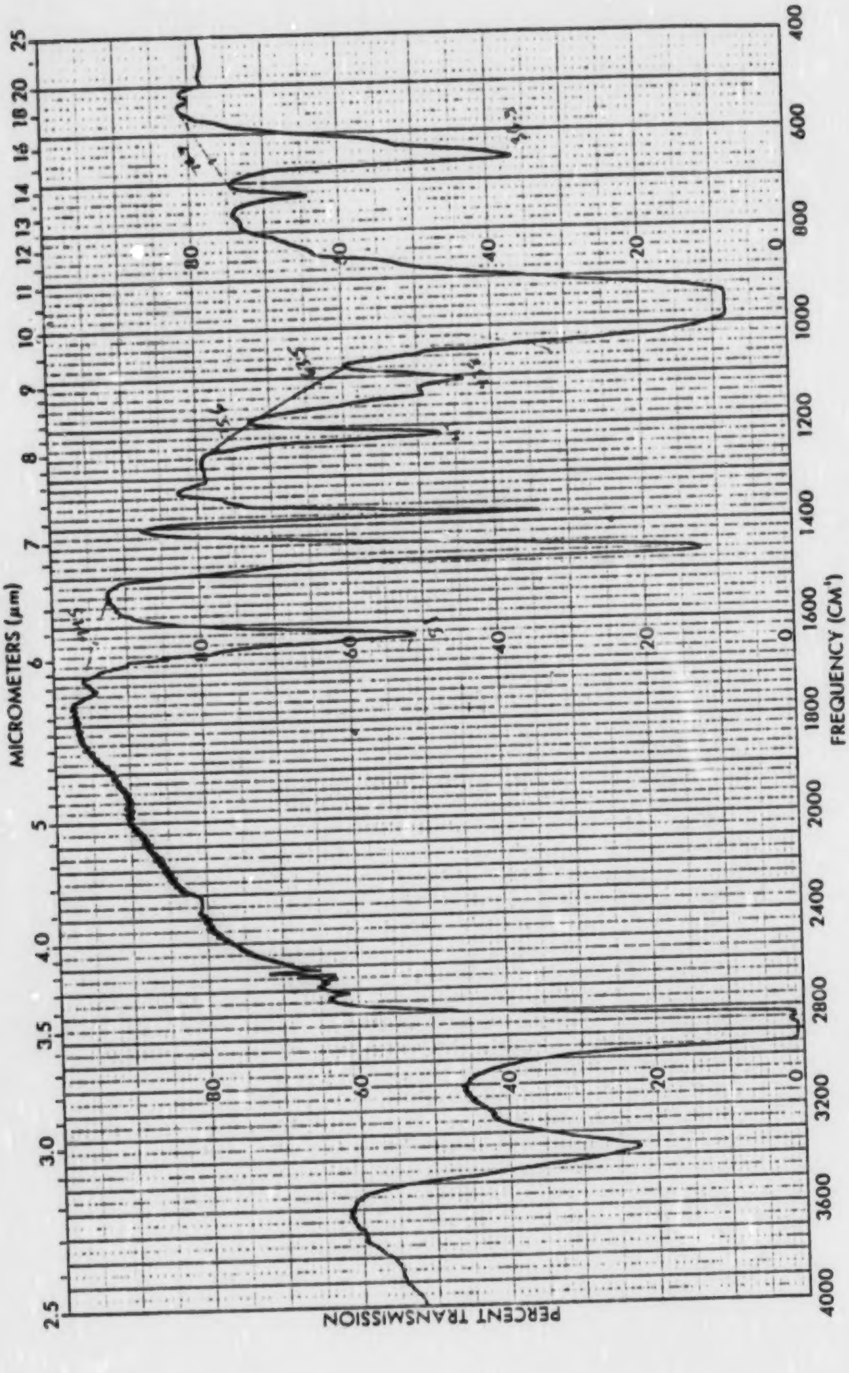


FIGURE F-19. INFRARED SPECTRA OF KINETIC RUN 16 PRECIPITATED SOLIDS

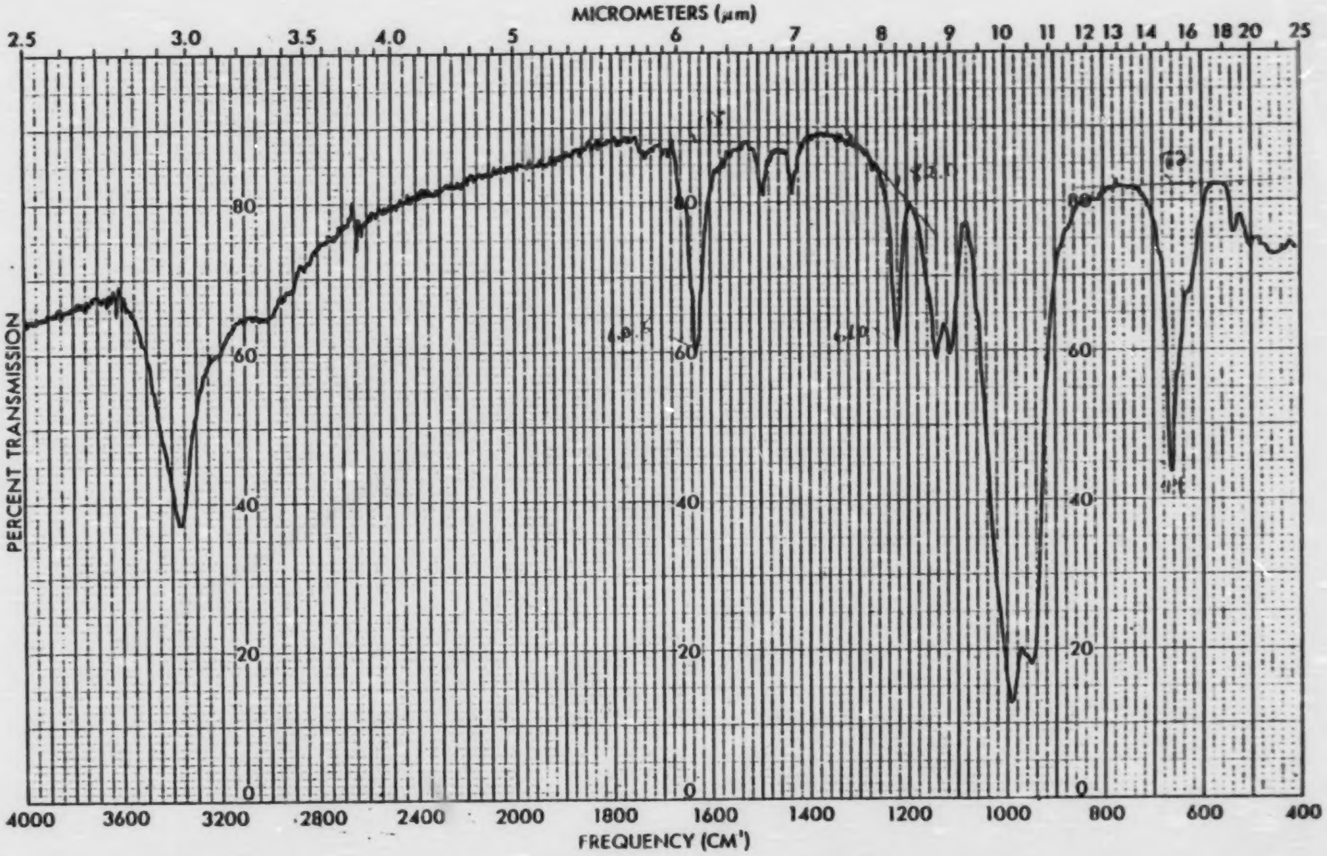


FIGURE F-20. INFRARED SPECTRA OF KINETIC RUN 16 PRECIPITATED SOLIDS

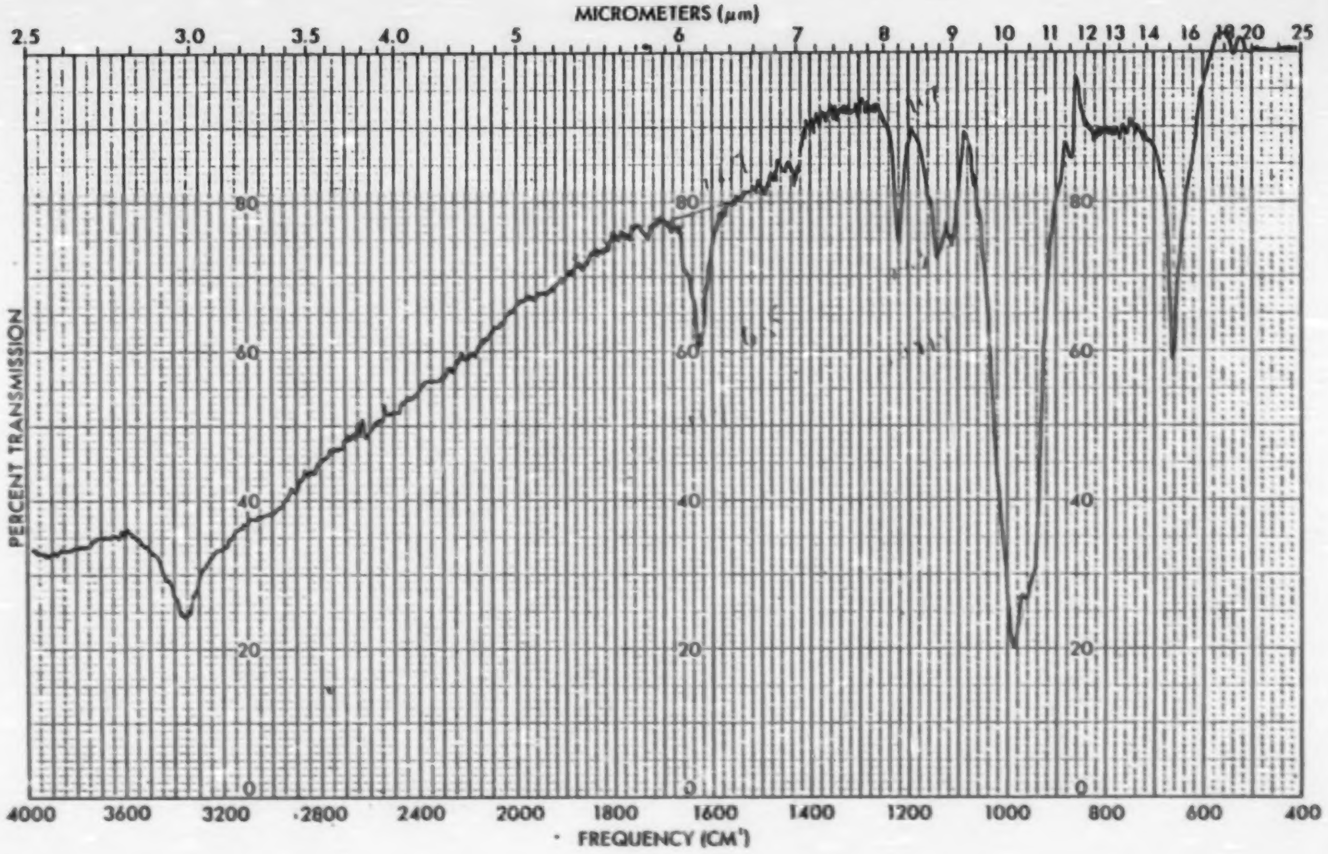


FIGURE F-21. INFRARED SPECTRA OF KINETIC RUN 17
PRECIPITATED SOLIDS

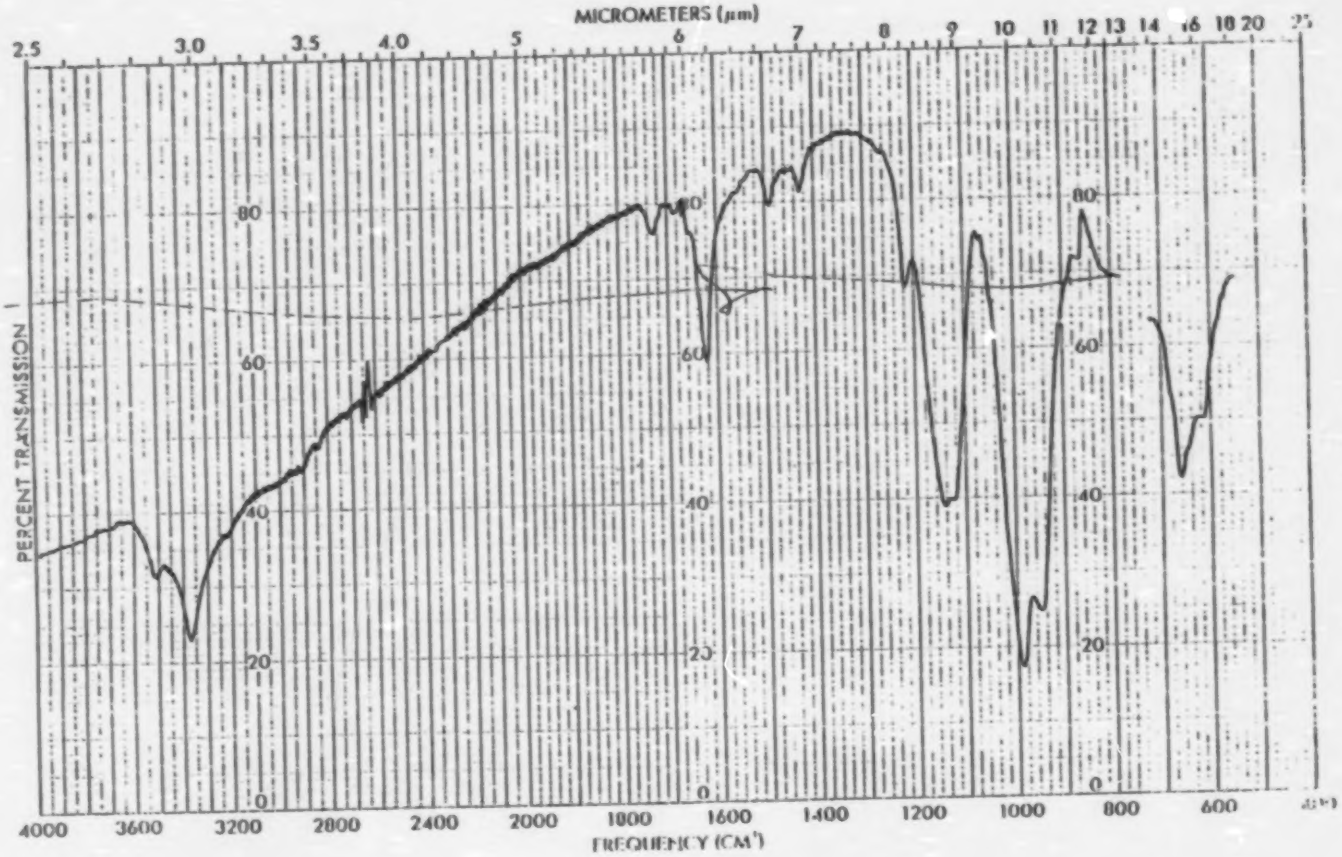


FIGURE F-22. INFRARED SPECTRA OF KINETIC RUN 20 PRECIPITATED SOLIDS

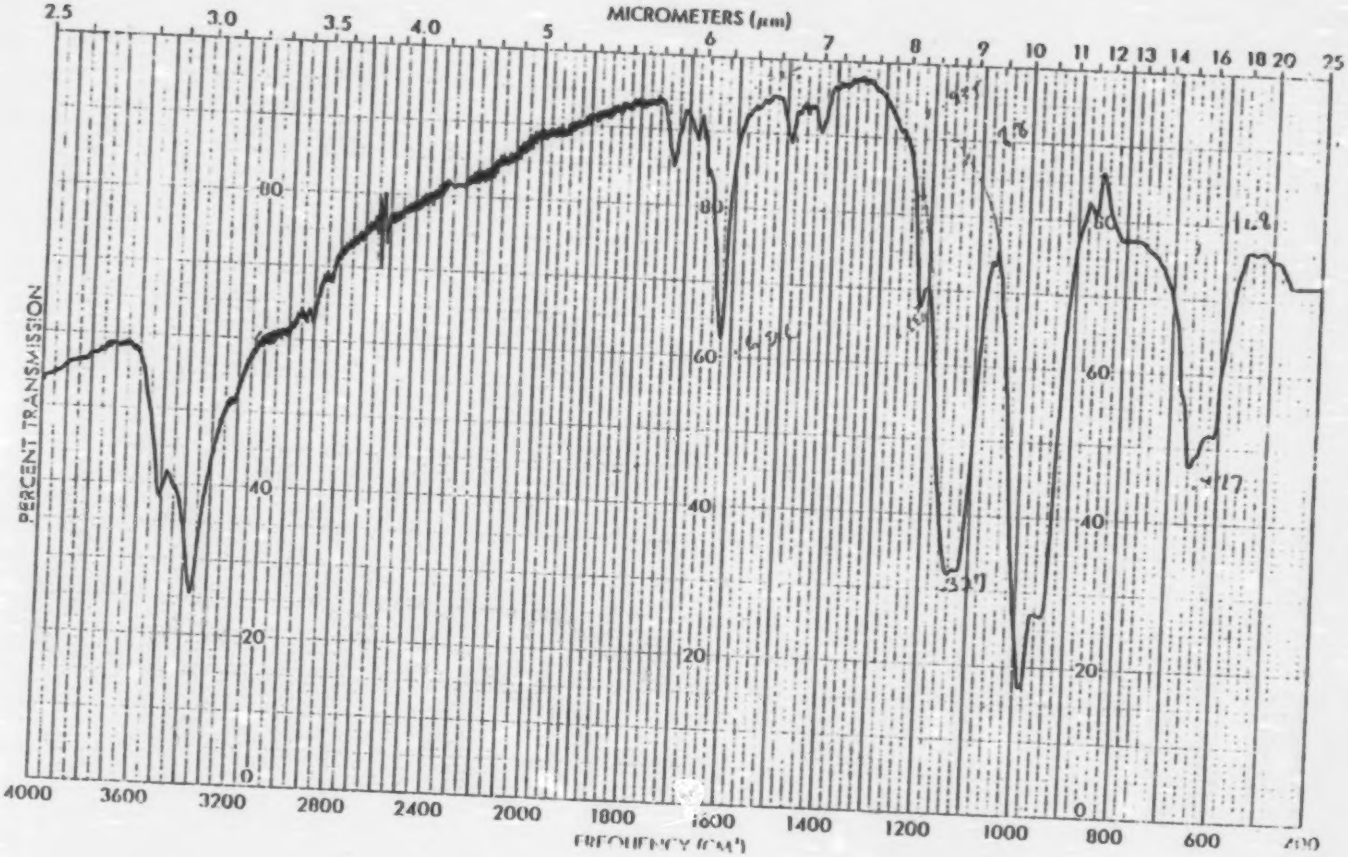


FIGURE F-23. INFRARED SPECTRA OF KINETIC RUN 20 PRECIPITATED SOLIDS

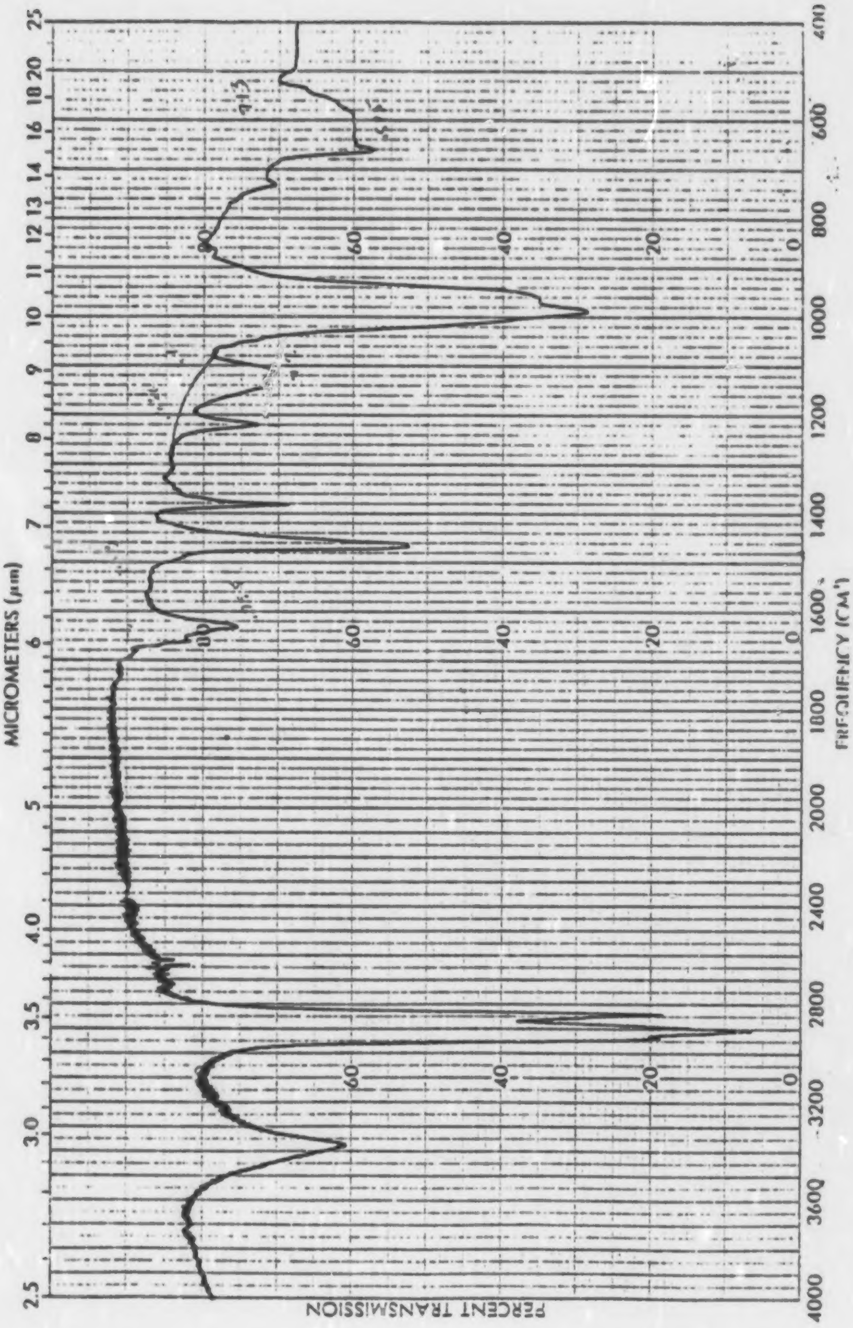


FIGURE F-24. INFRARED SPECTRA OF KINETIC RUNS 19 AND 20 AFTER EQUILIBRATION WITH MOTHER LIQUOR

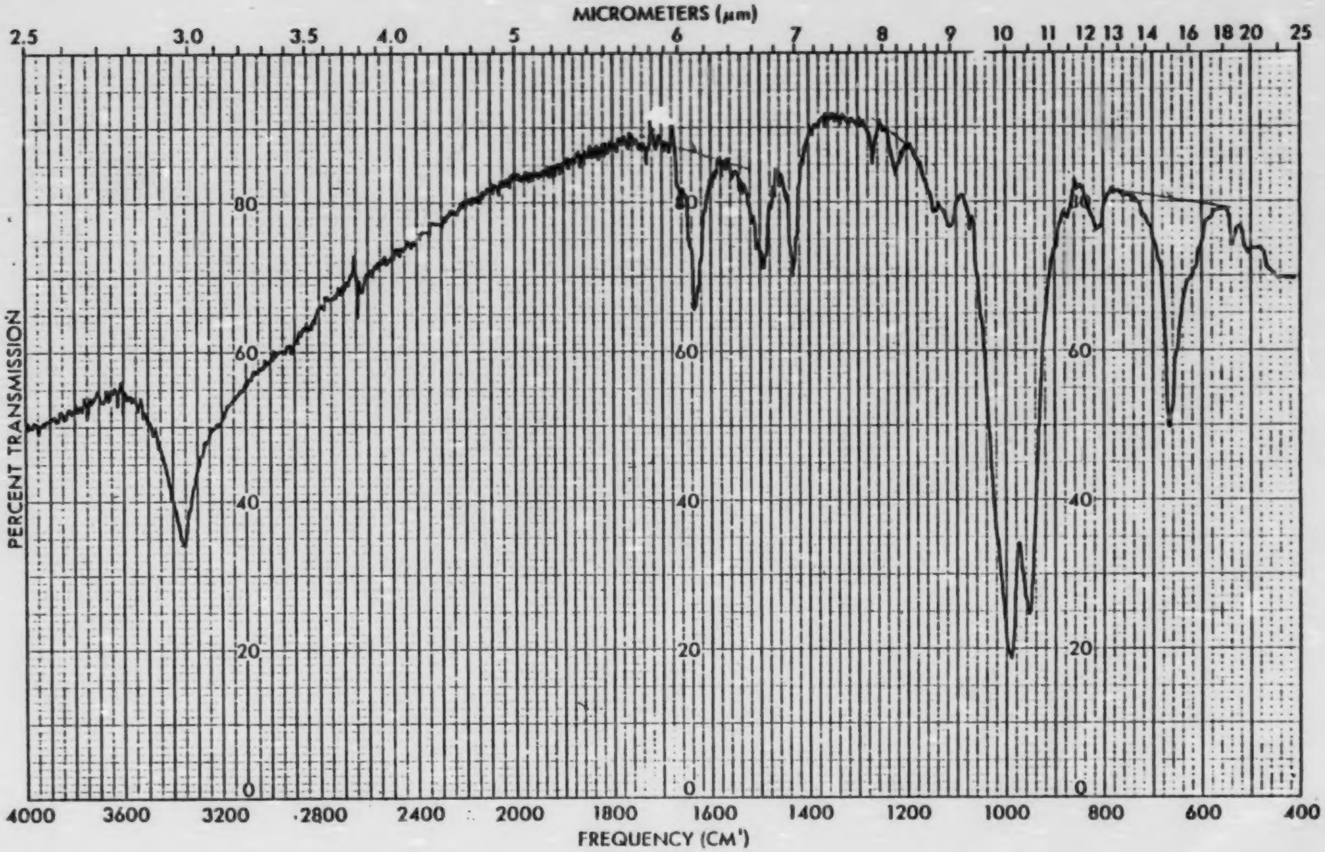


FIGURE F-25. INFRARED SPECTRA OF KINETIC RUN 22 PRECIPITATED SOLIDS

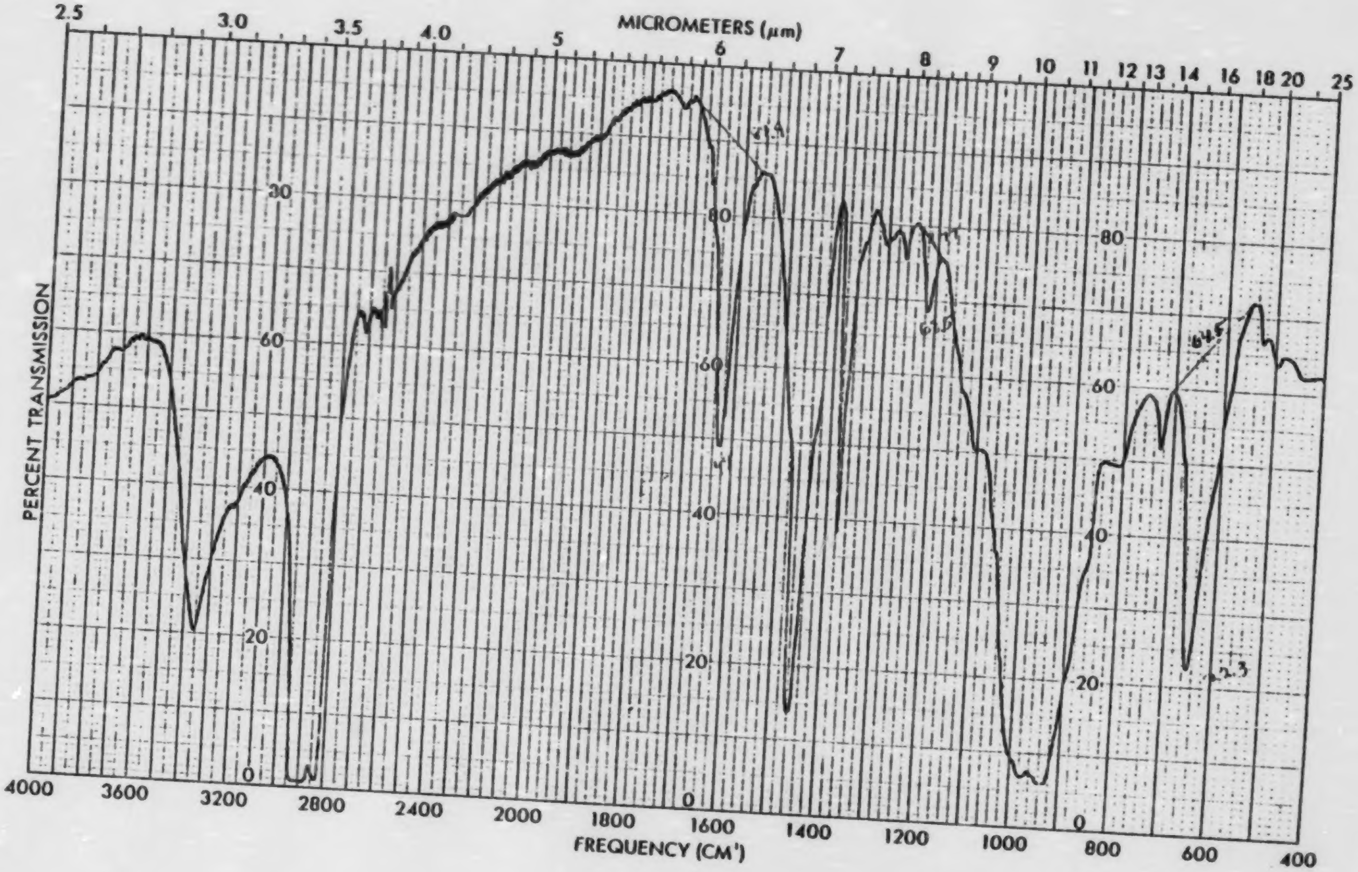


FIGURE F-26. INFRARED SPECTRA OF KINETIC RUN 22 PRECIPITATED SOLIDS

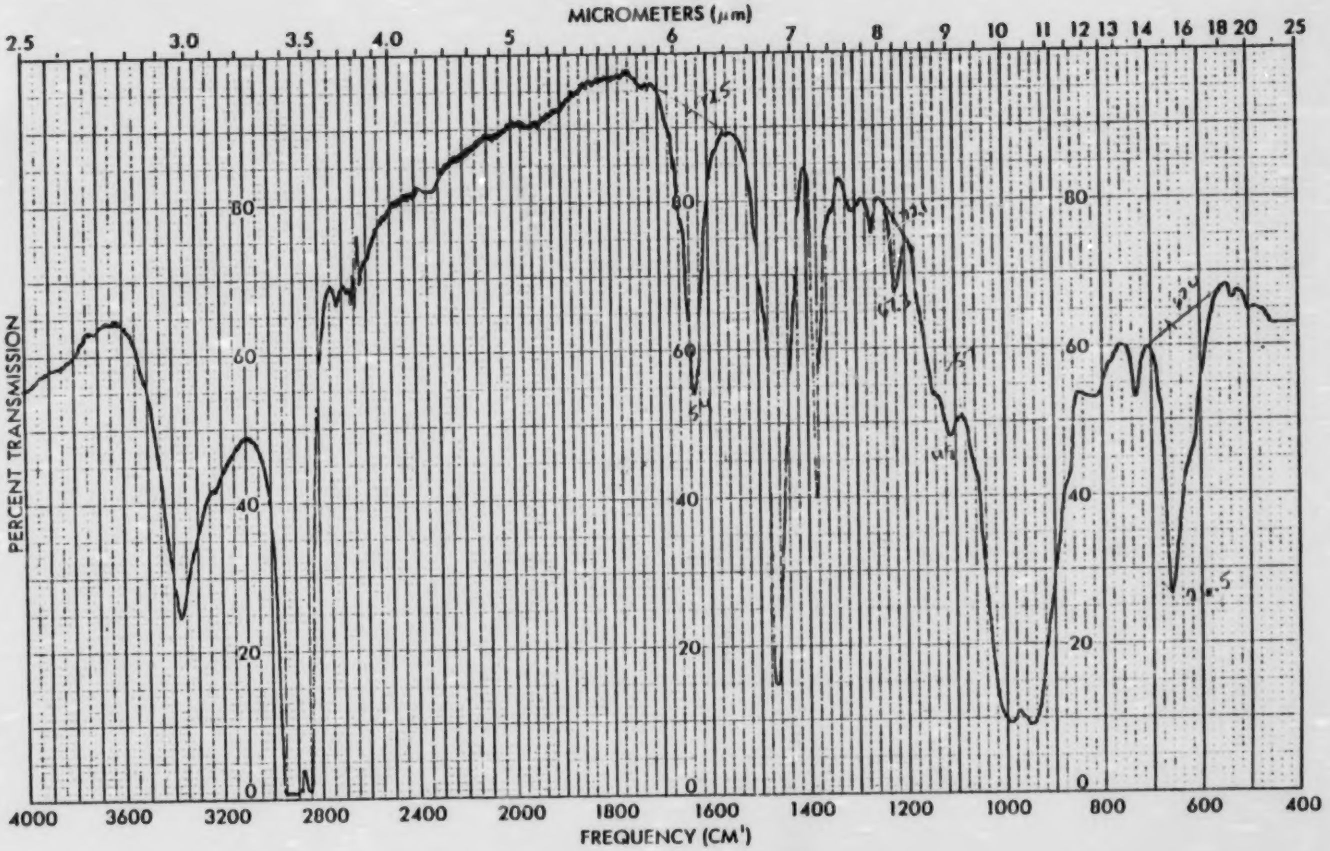


FIGURE F-27. INFRARED SPECTRA OF KINETIC RUN 23
PRECIPITATED SOLIDS

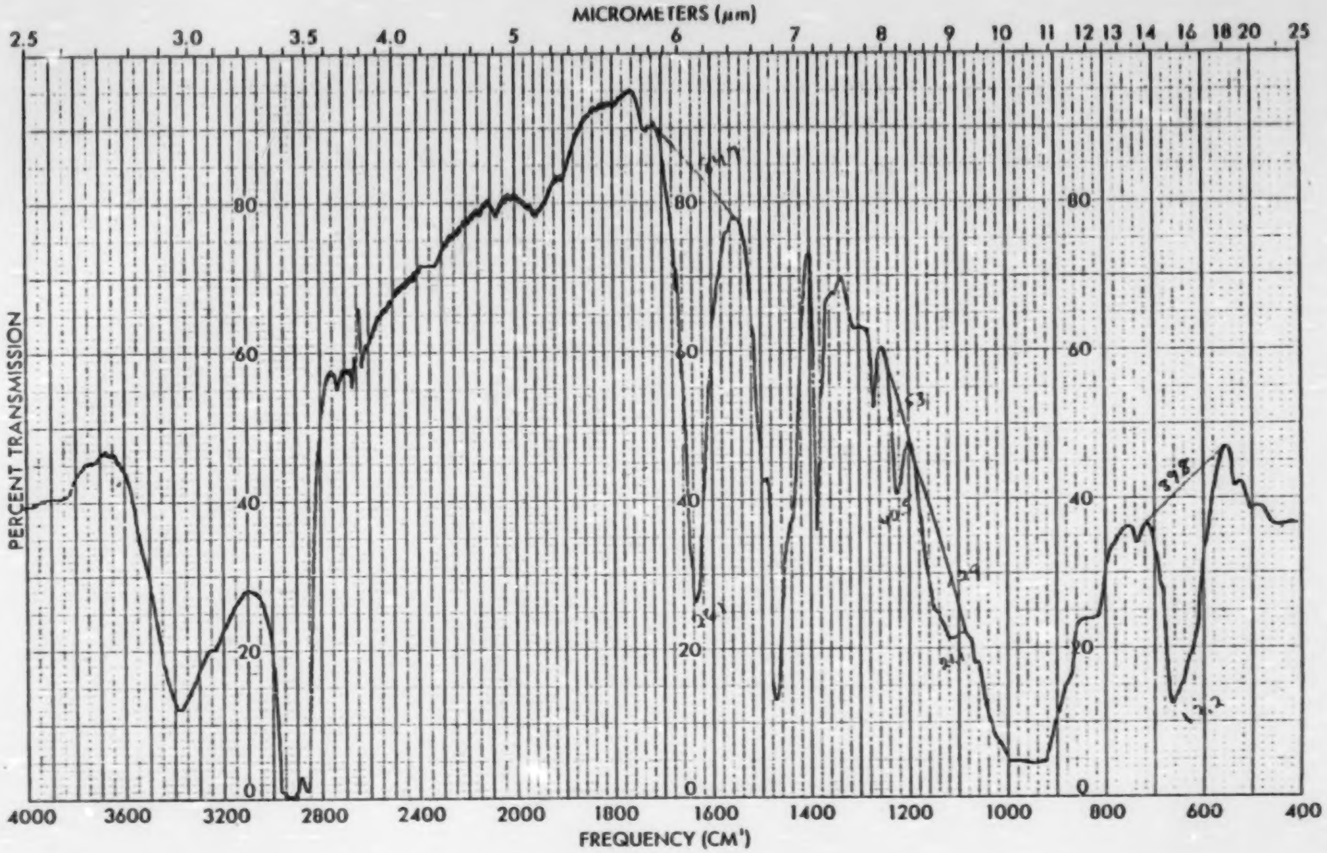


FIGURE F-28. INFRARED SPECTRA OF KINETIC RUN 23 PRECIPITATED SOLIDS

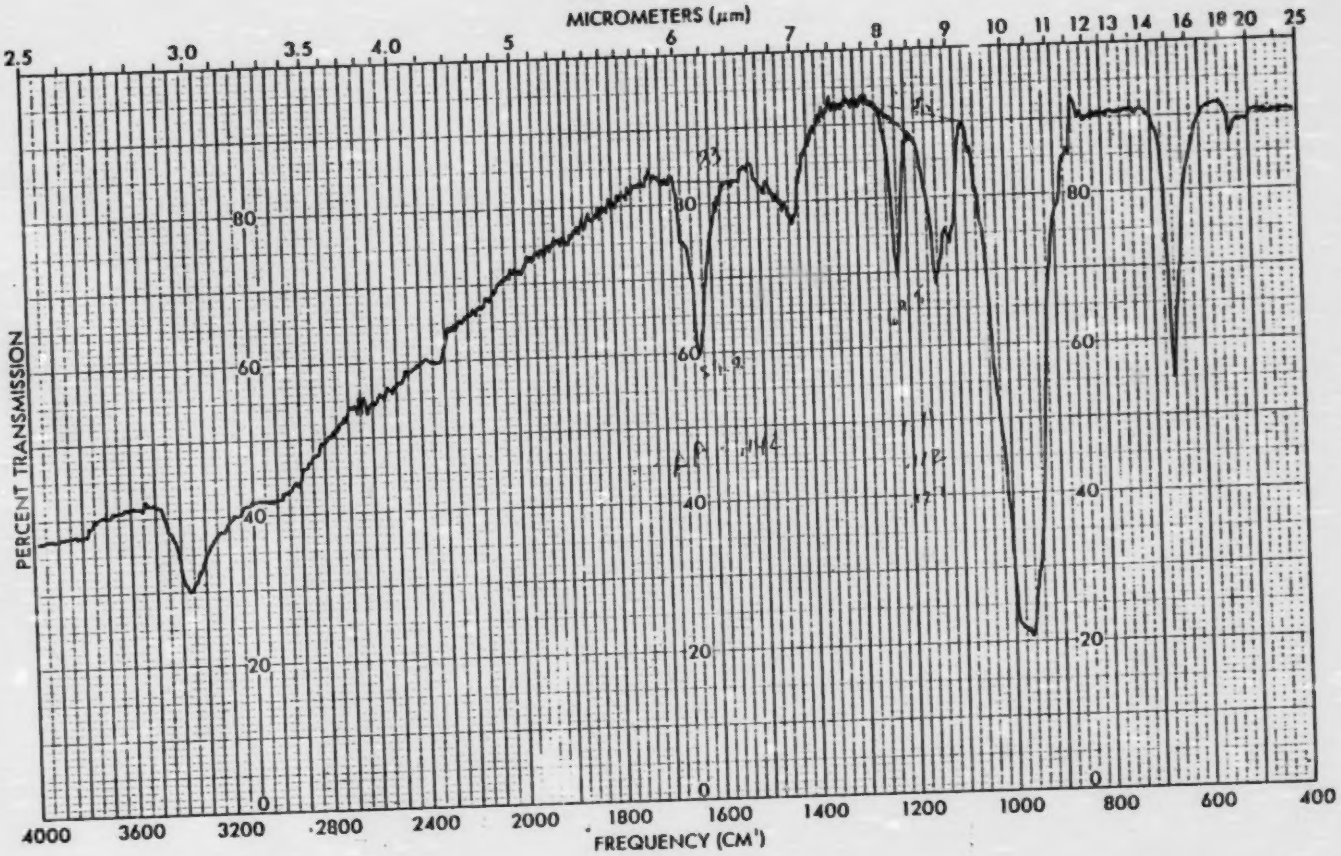


FIGURE F-29. INFRARED SPECTRA OF KINETIC RUN 24
PRECIPITATED SOLIDS

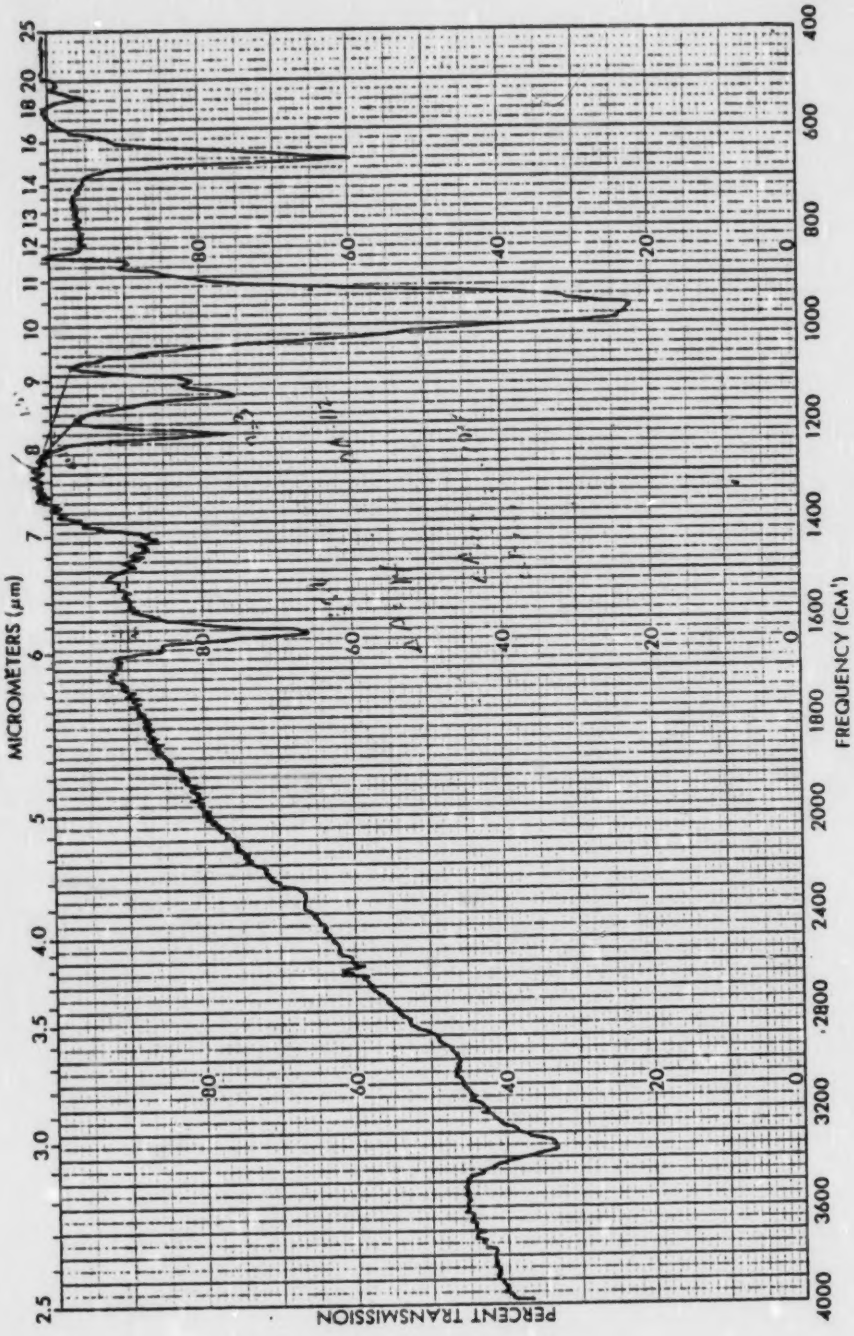


FIGURE F-30. INFRARED SPECTRA OF KINETIC RUN 24 PRECIPITATED SOLIDS

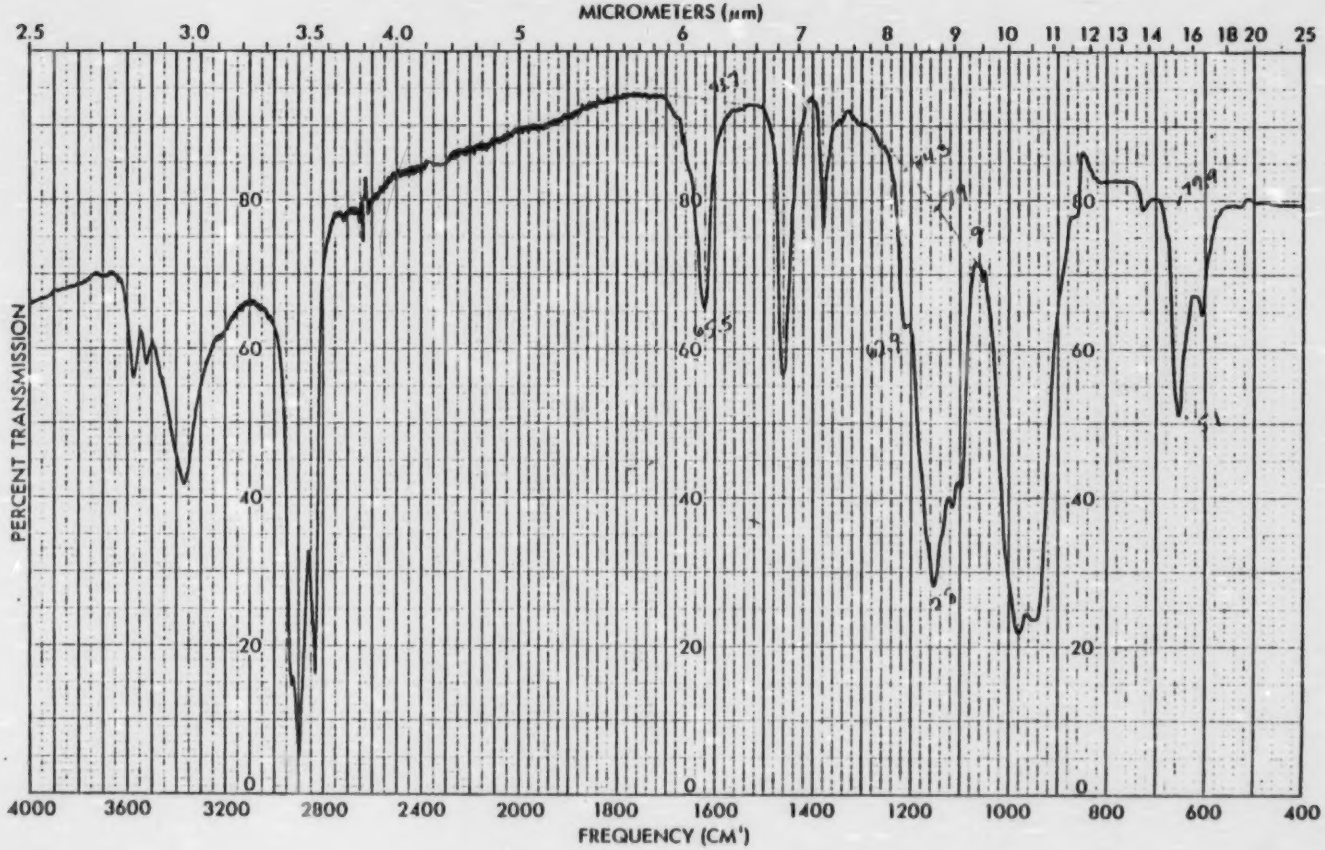


FIGURE F-31. INFRARED SPECTRA OF KINETIC RUN 26
PRECIPITATED SOLIDS

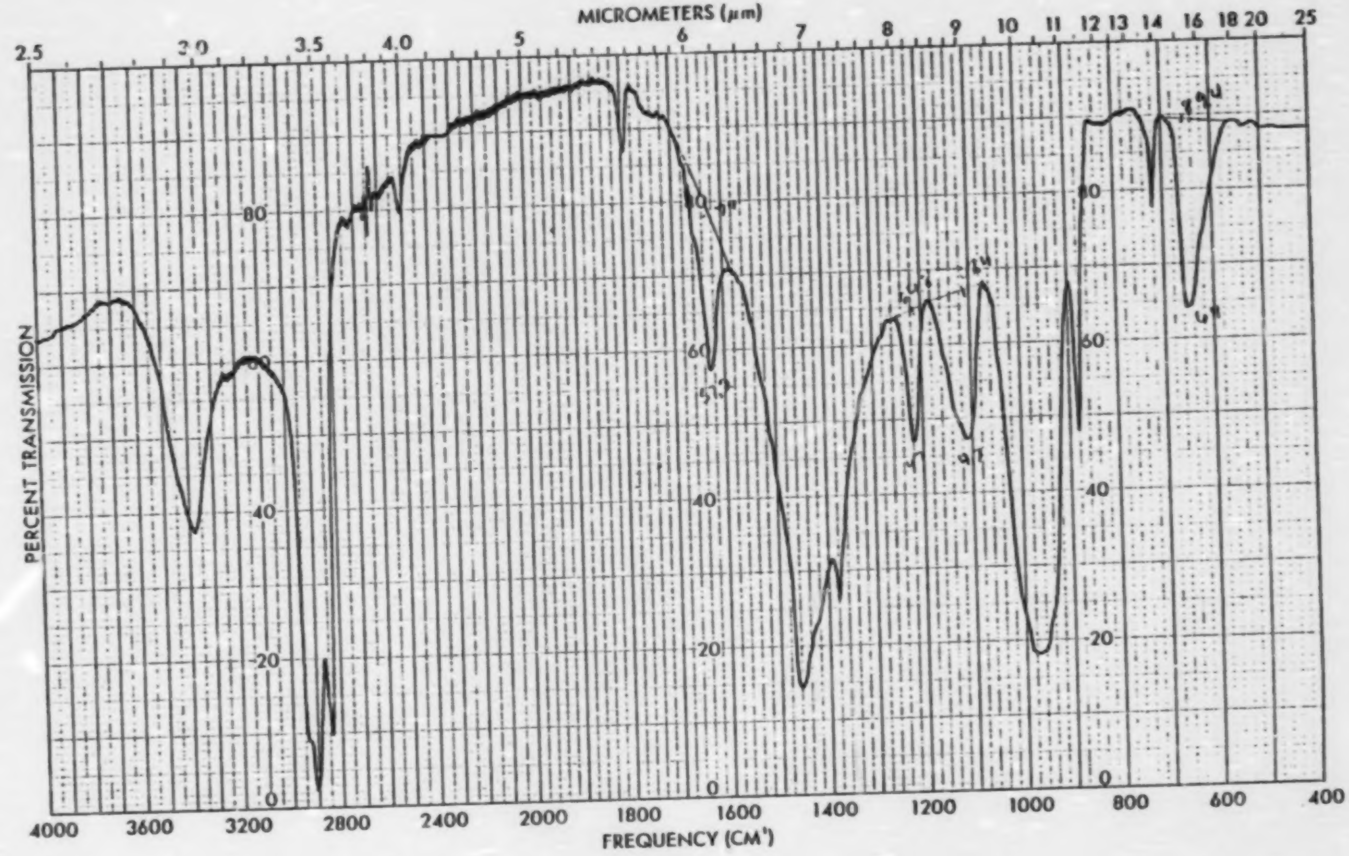


FIGURE F-32. INFRARED SPECTRA OF KINETIC RUN 32 PRECIPITATED SOLIDS

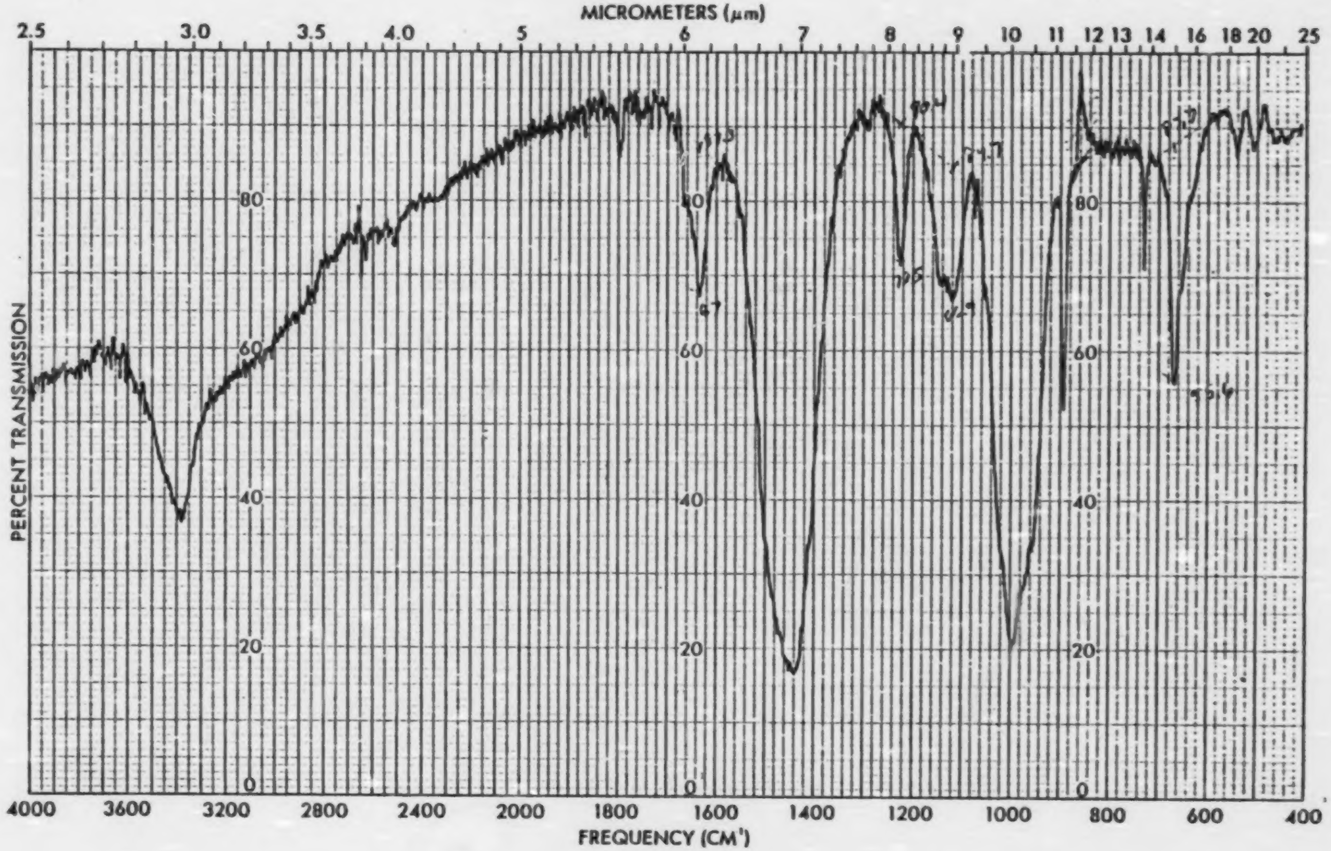


FIGURE F-33. INFRARED SPECTRA OF KINETIC RUN 33 PRECIPITATED SOLIDS

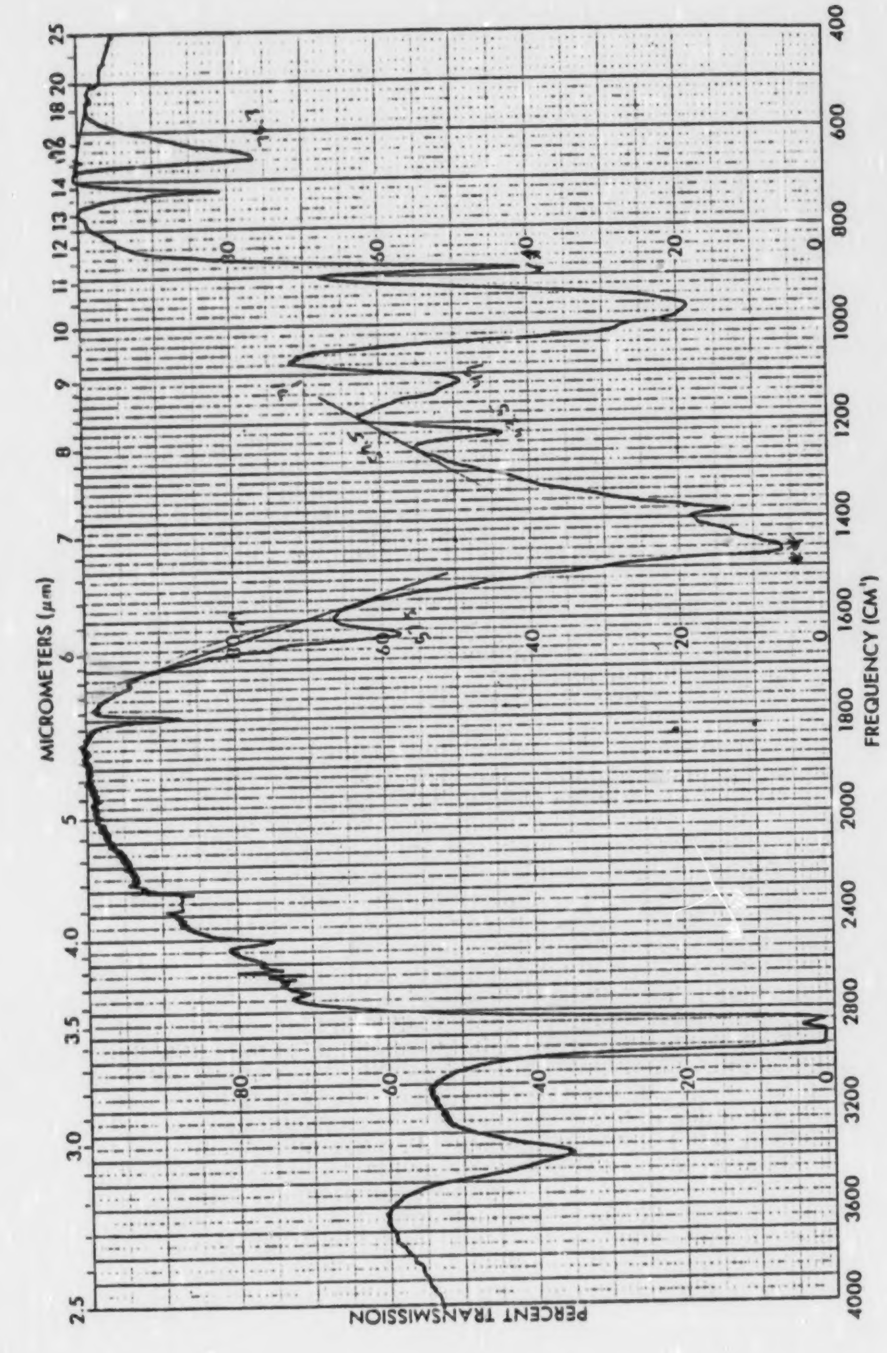


FIGURE F-34. INFRARED SPECTRA OF KINETIC RUN 34 PRECIPITATED SOLIDS

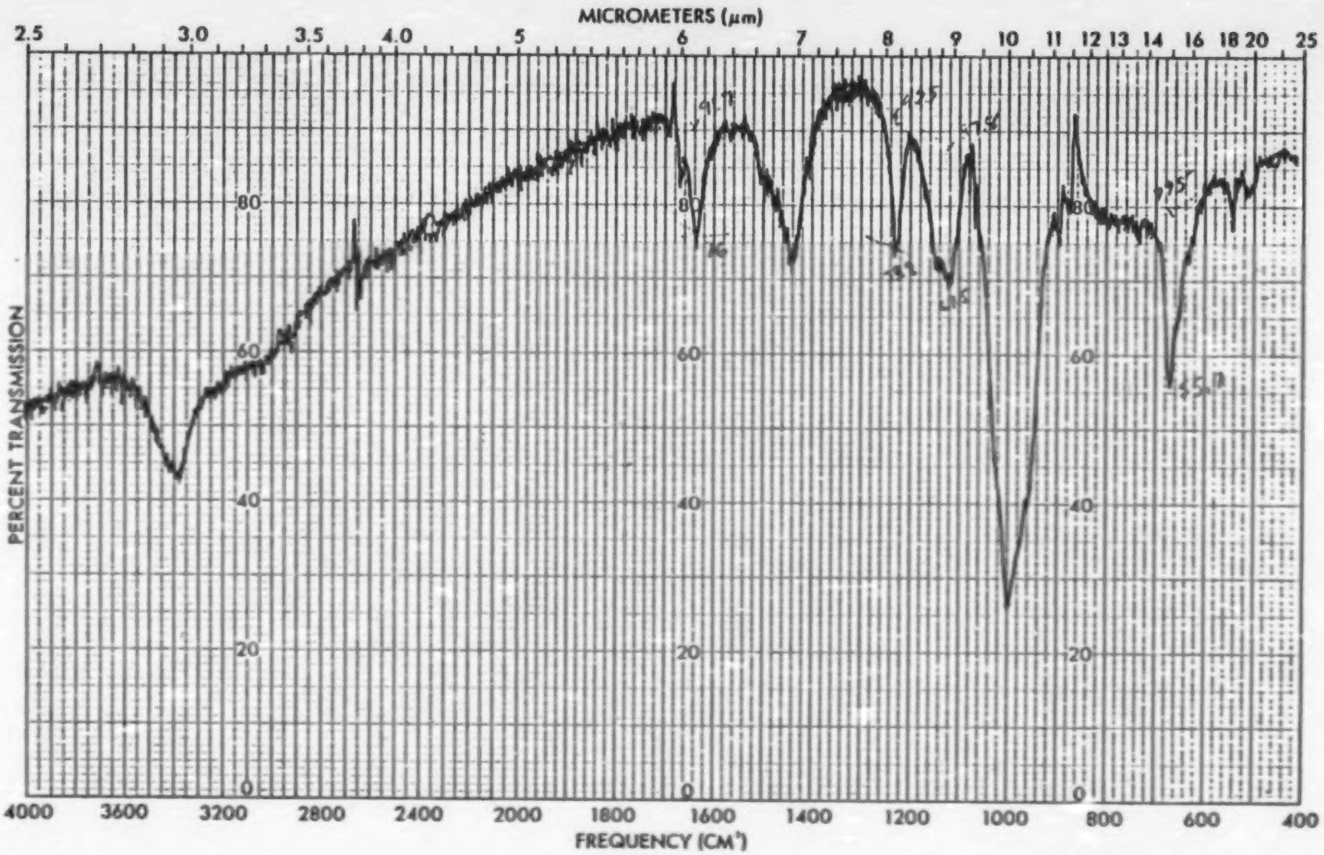


FIGURE F-35. INFRARED SPECTRA OF KINETIC RUN 35 PRECIPITATED SOLIDS

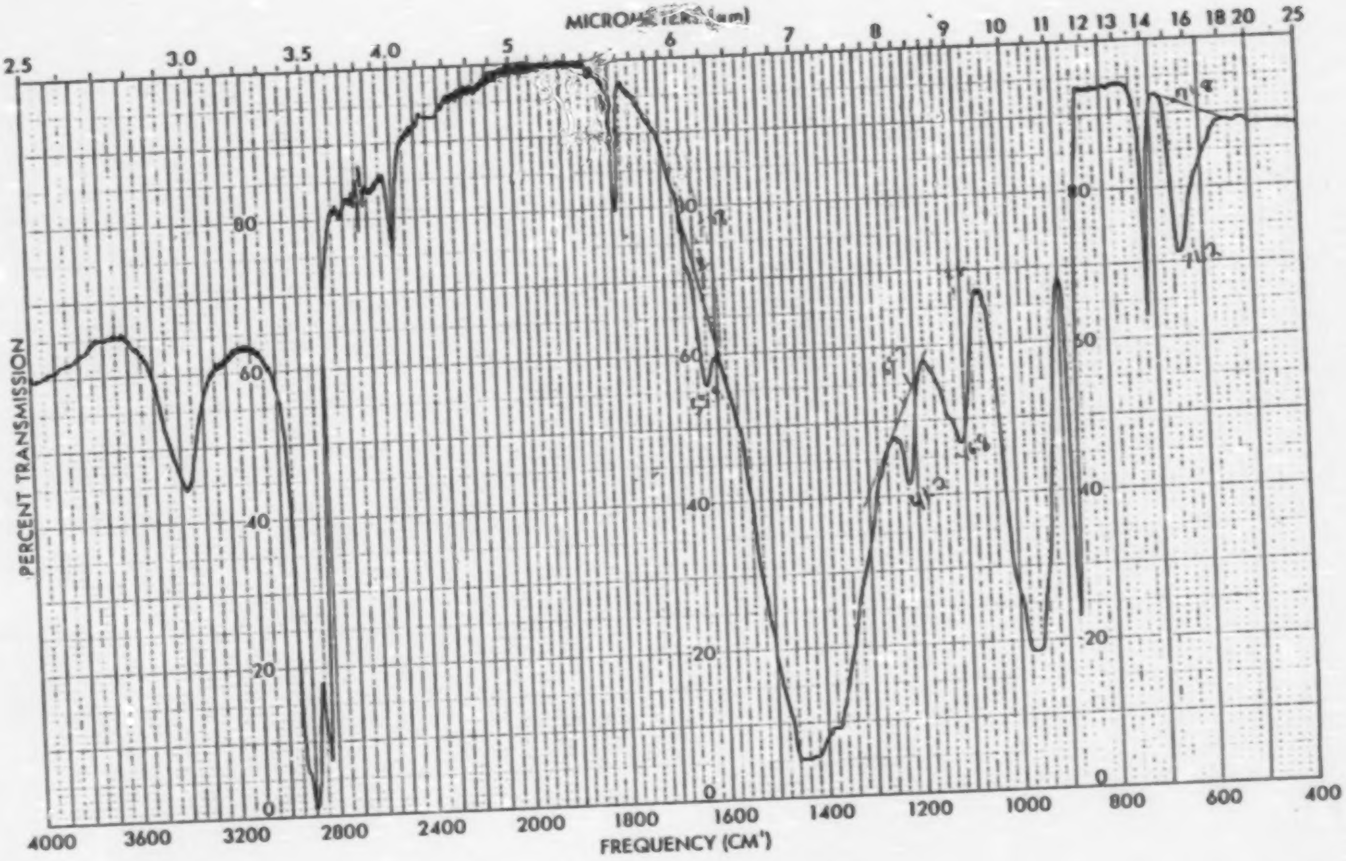


FIGURE F-36. INFRARED SPECTRA OF KINETIC RUN 35 PRECIPITATED SOLIDS

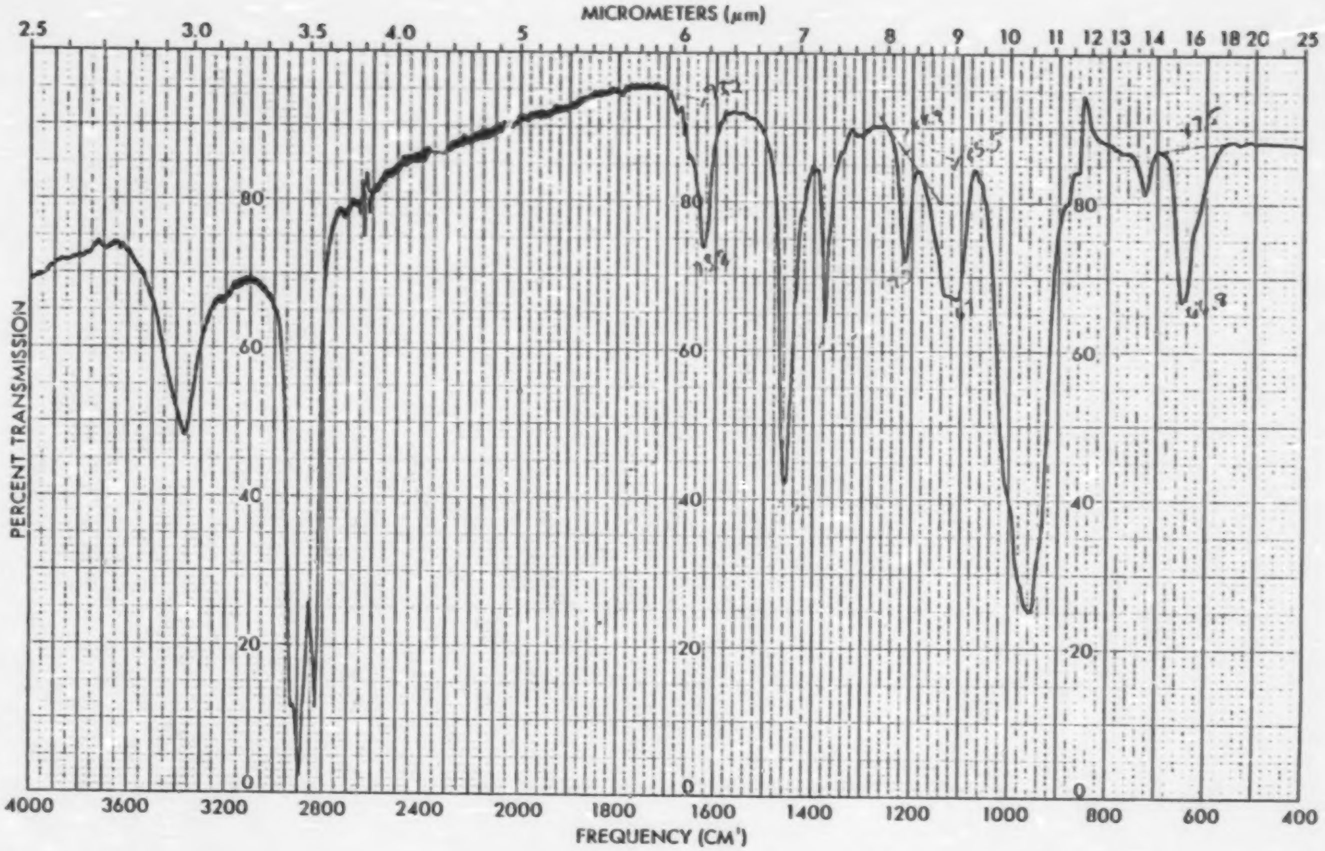


FIGURE F-37. INFRARED SPECTRA OF KINETIC RUN 37
PRECIPITATED SOLIDS

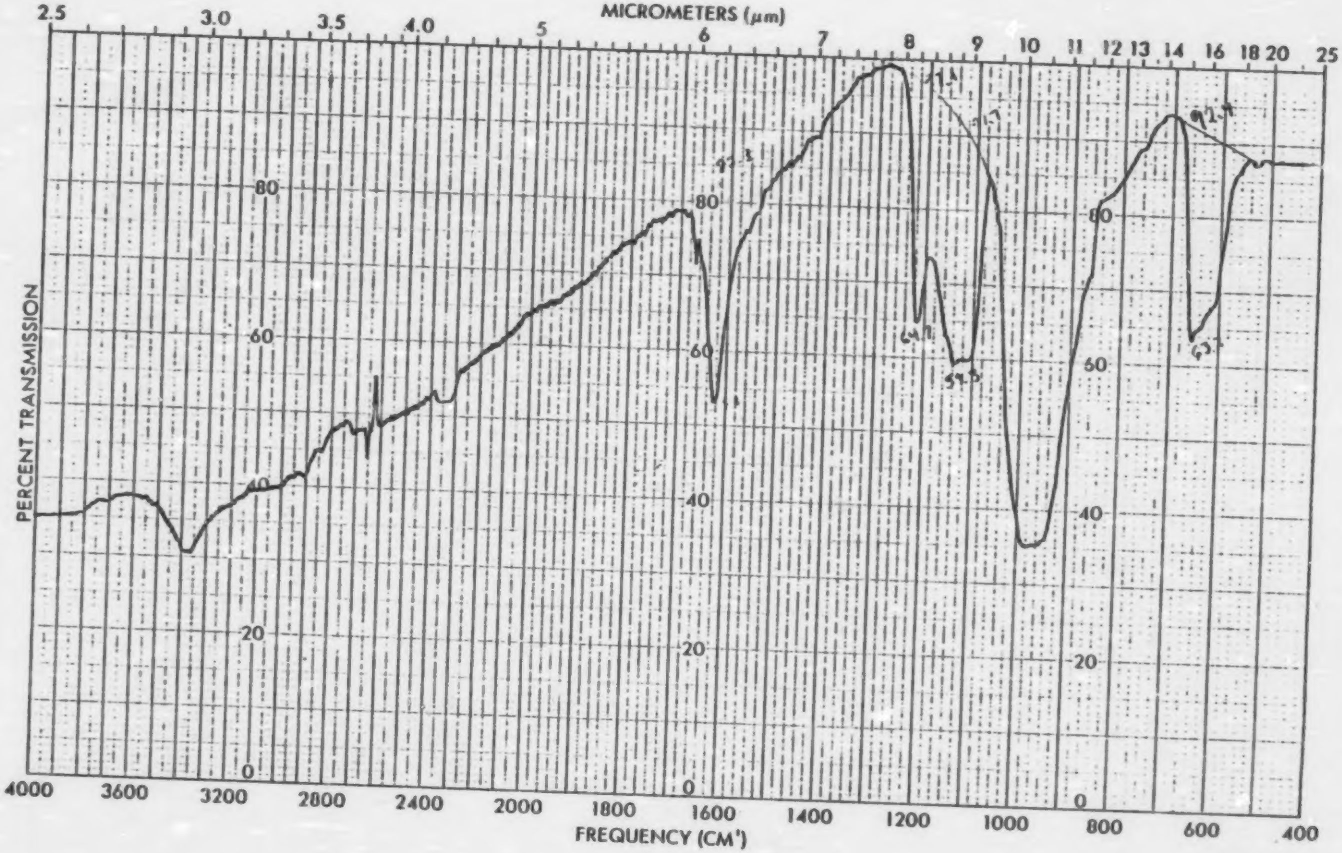


FIGURE F-38. INFRARED SPECTRA OF KINETIC RUN 38
PRECIPITATED SOLIDS

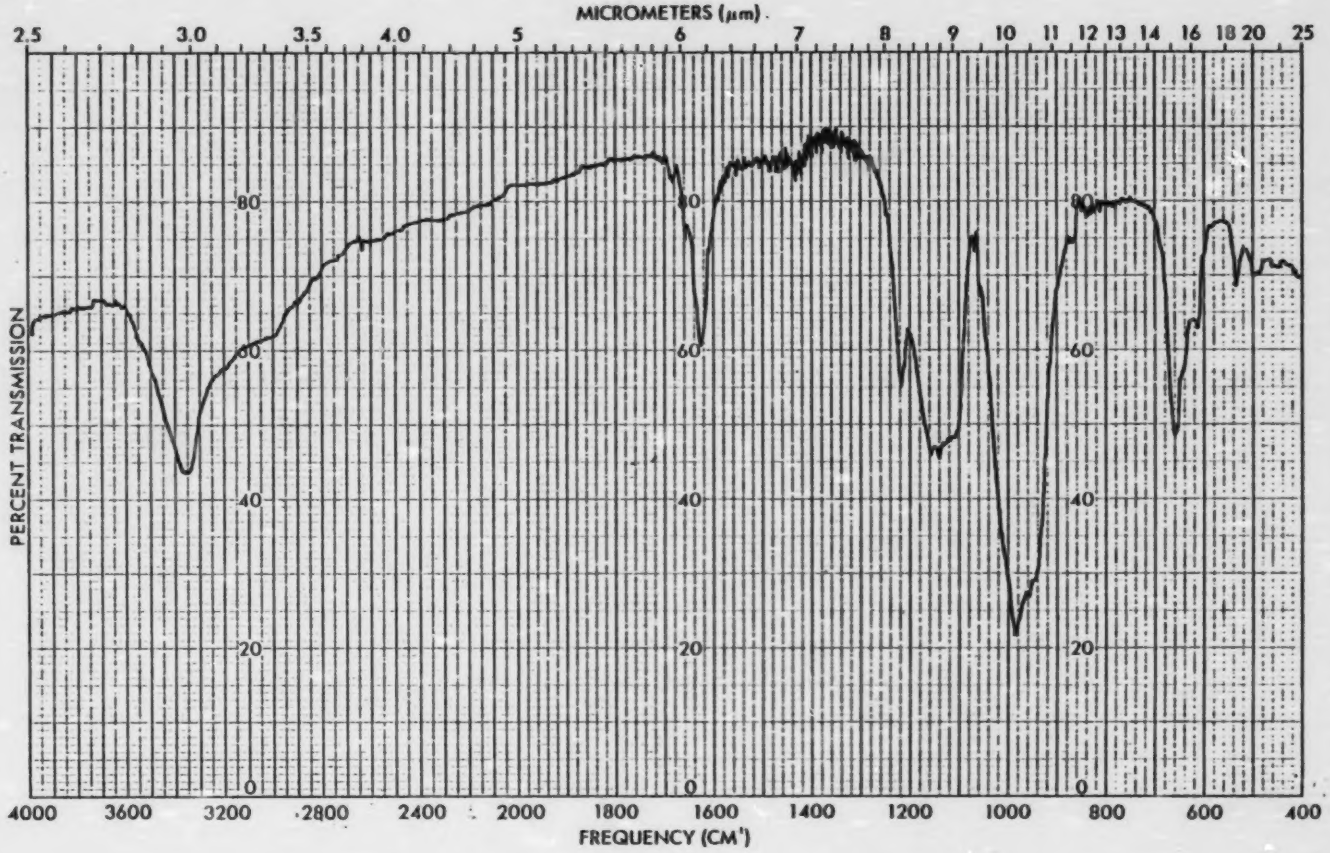


FIGURE F-39. INFRARED SPECTRA OF KINETIC RUN 39
PRECIPITATED SOLIDS

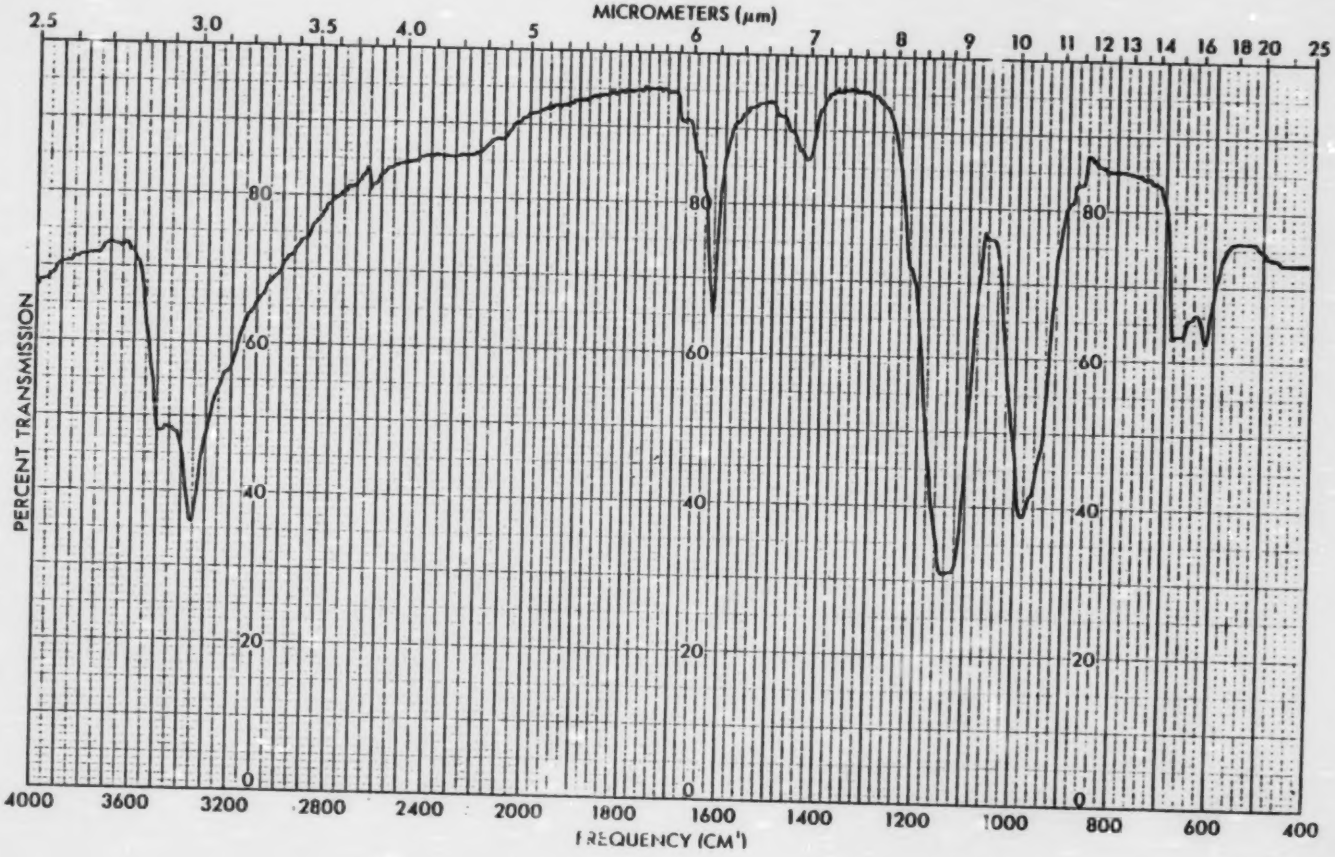


FIGURE F-40. INFRARED SPECTRA OF KINETIC RUN 39 PRECIPITATED SOLIDS

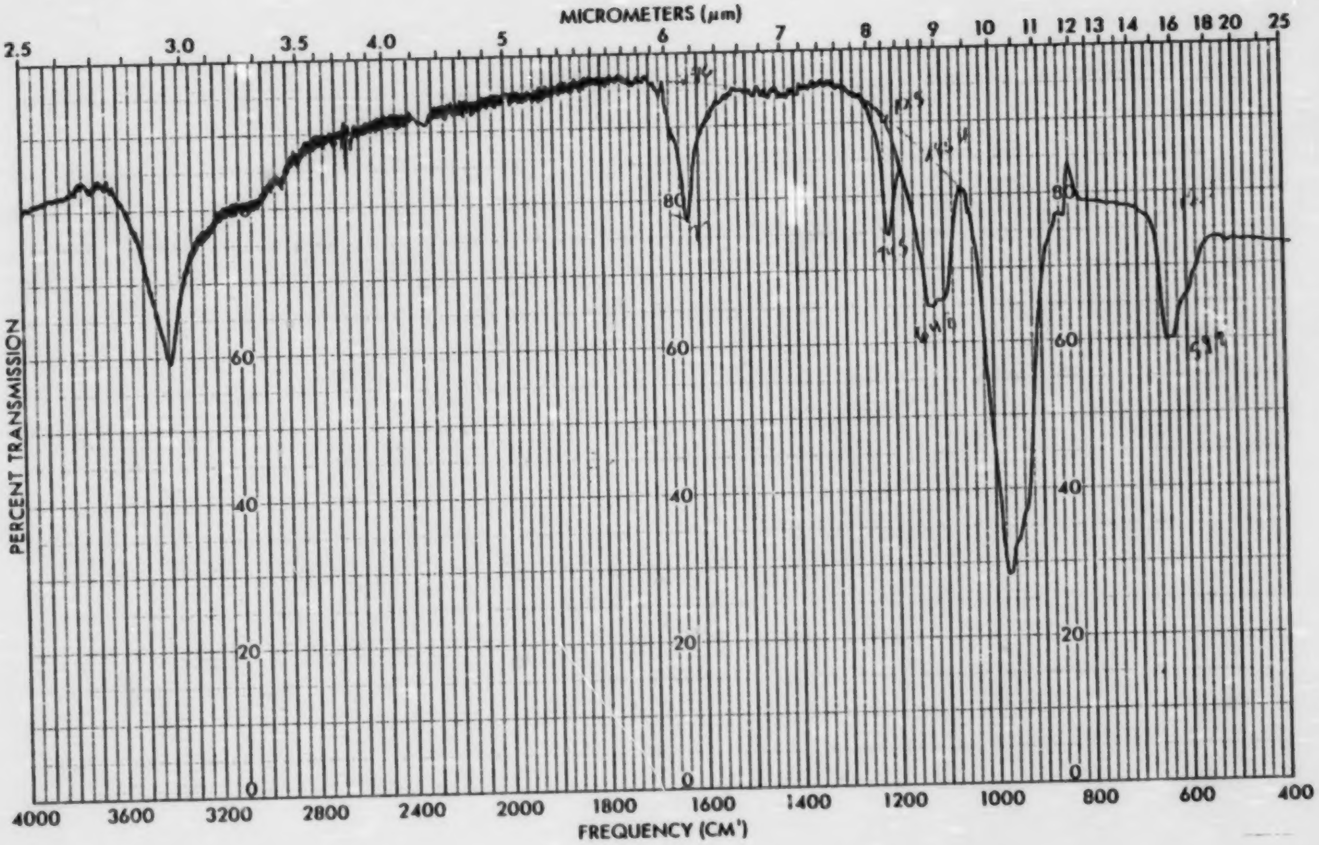


FIGURE F-41. INFRARED SPECTRA OF KINETIC RUN 39 PRECIPITATED SOLIDS

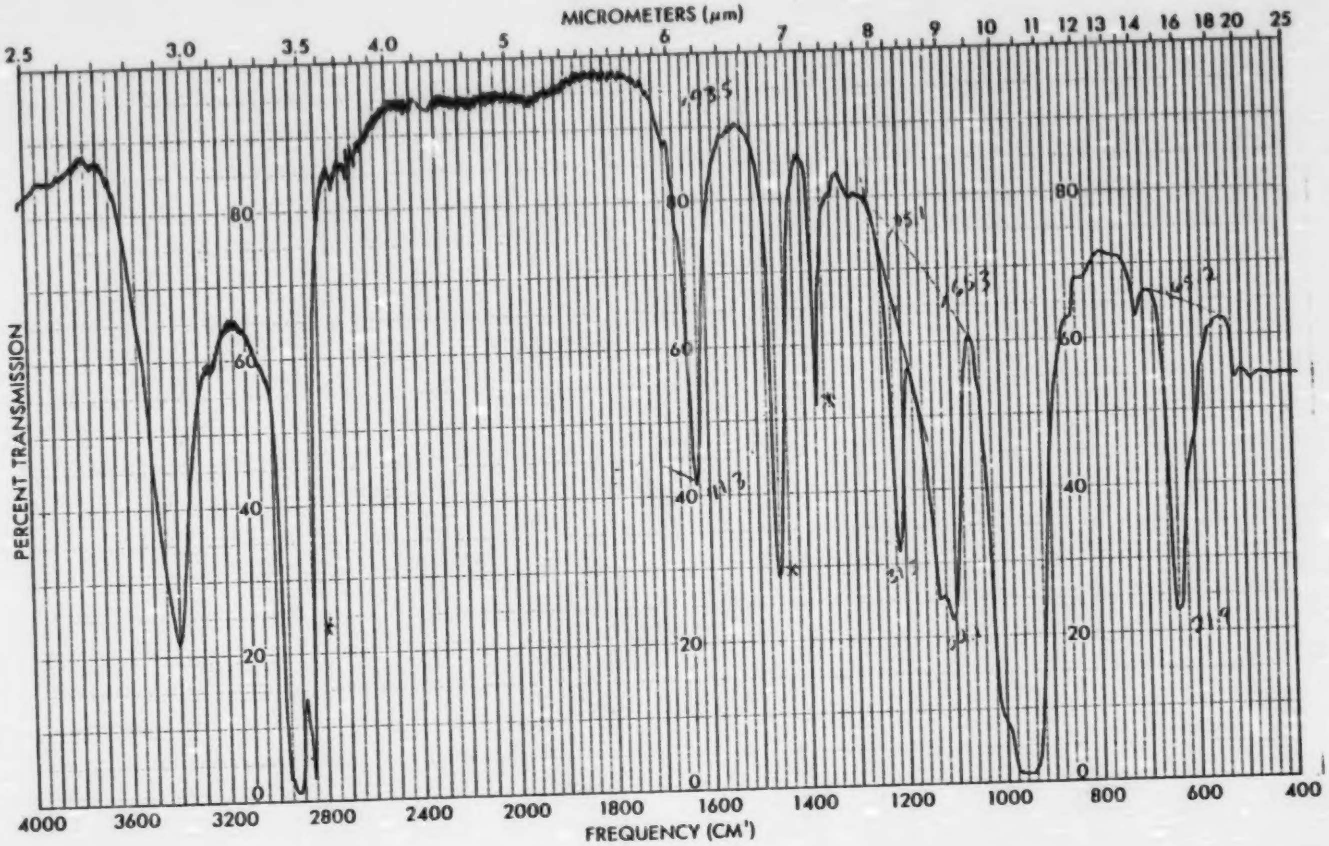


FIGURE F-42. INFRARED SPECTRA OF KINETIC RUN 39 PRECIPITATED SOLIDS

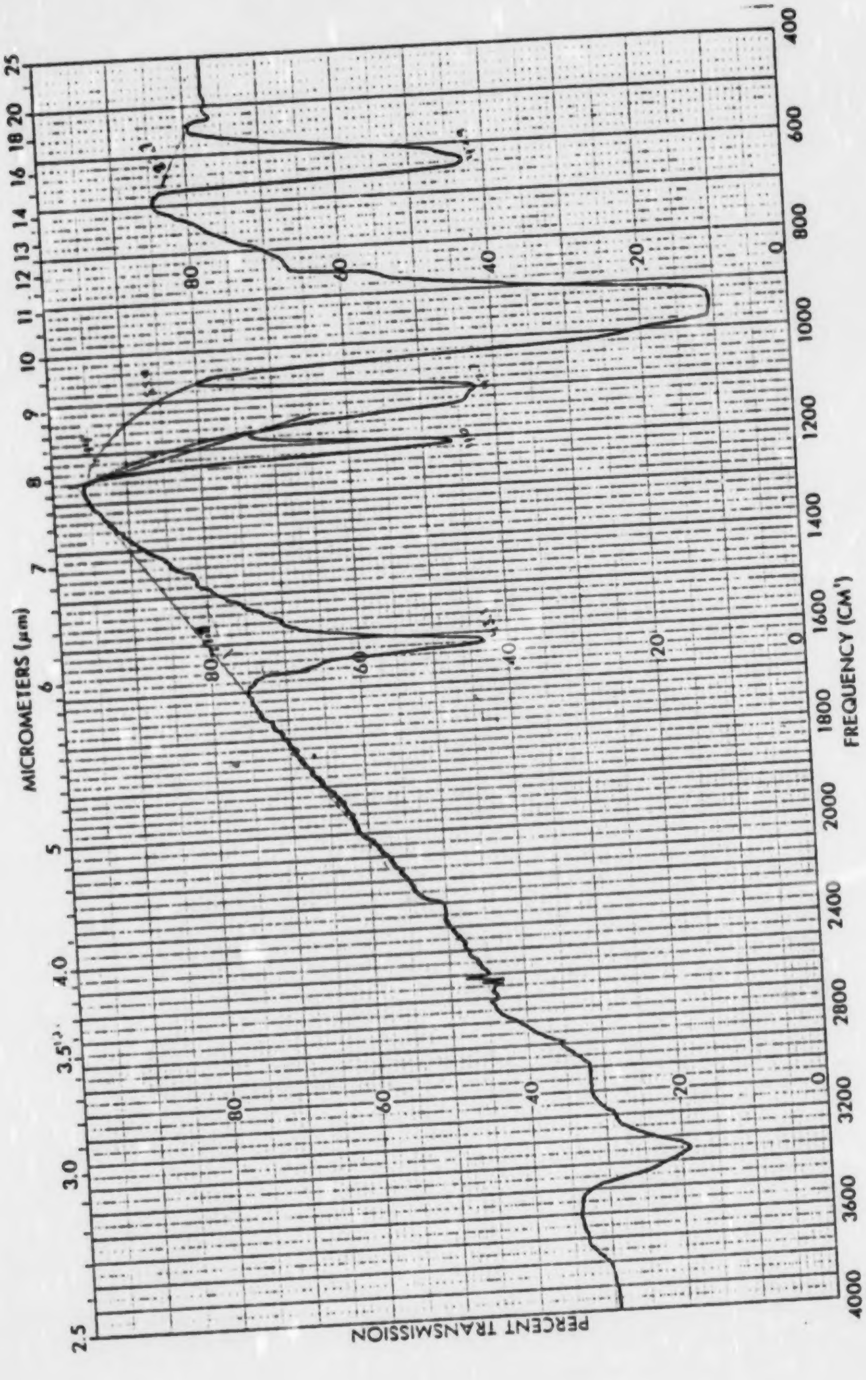


FIGURE F-43. INFRARED SPECTRA OF KINETIC RUN 41 PRECIPITATED SOLIDS

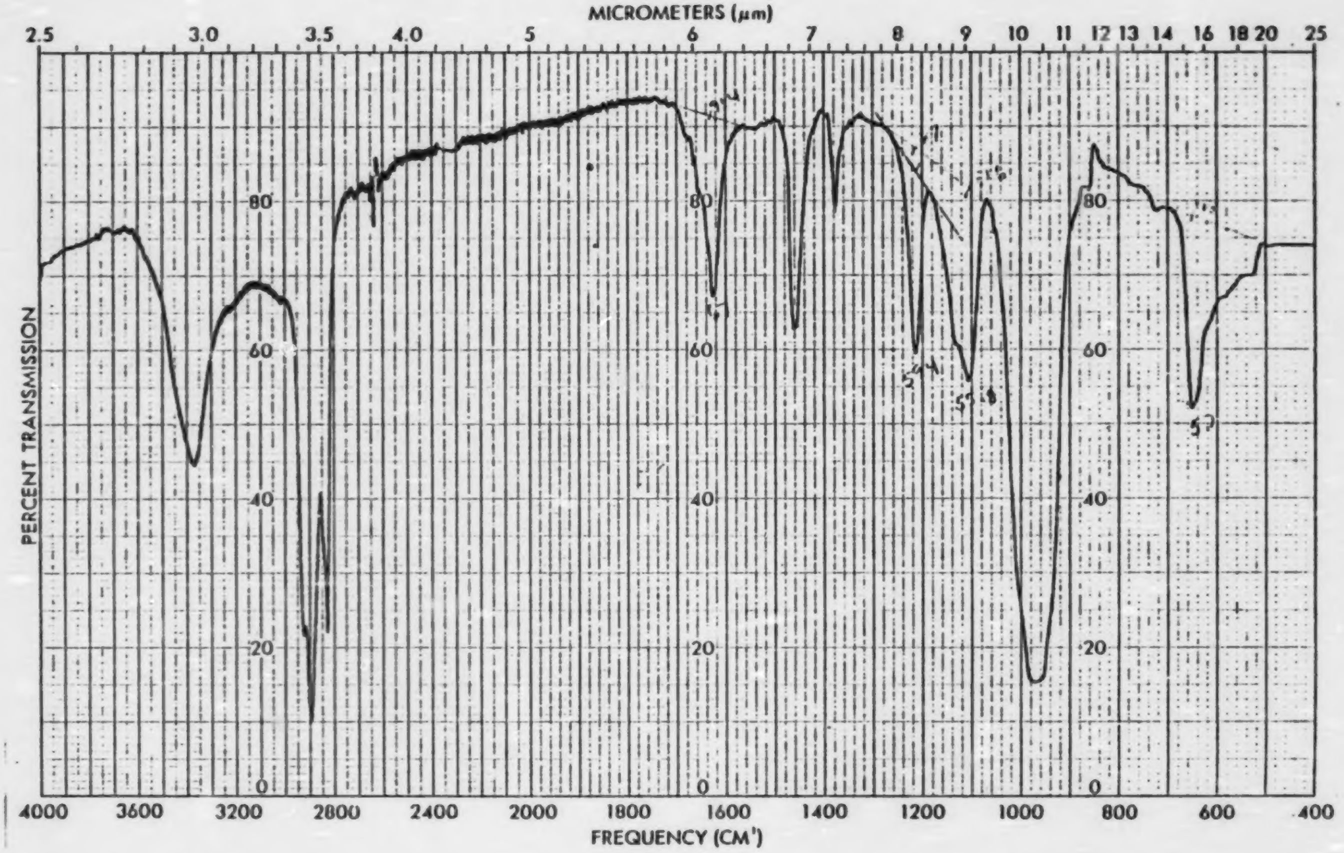


FIGURE F-44. INFRARED SPECTRA OF KINETIC RUN 42 PRECIPITATED SOLIDS

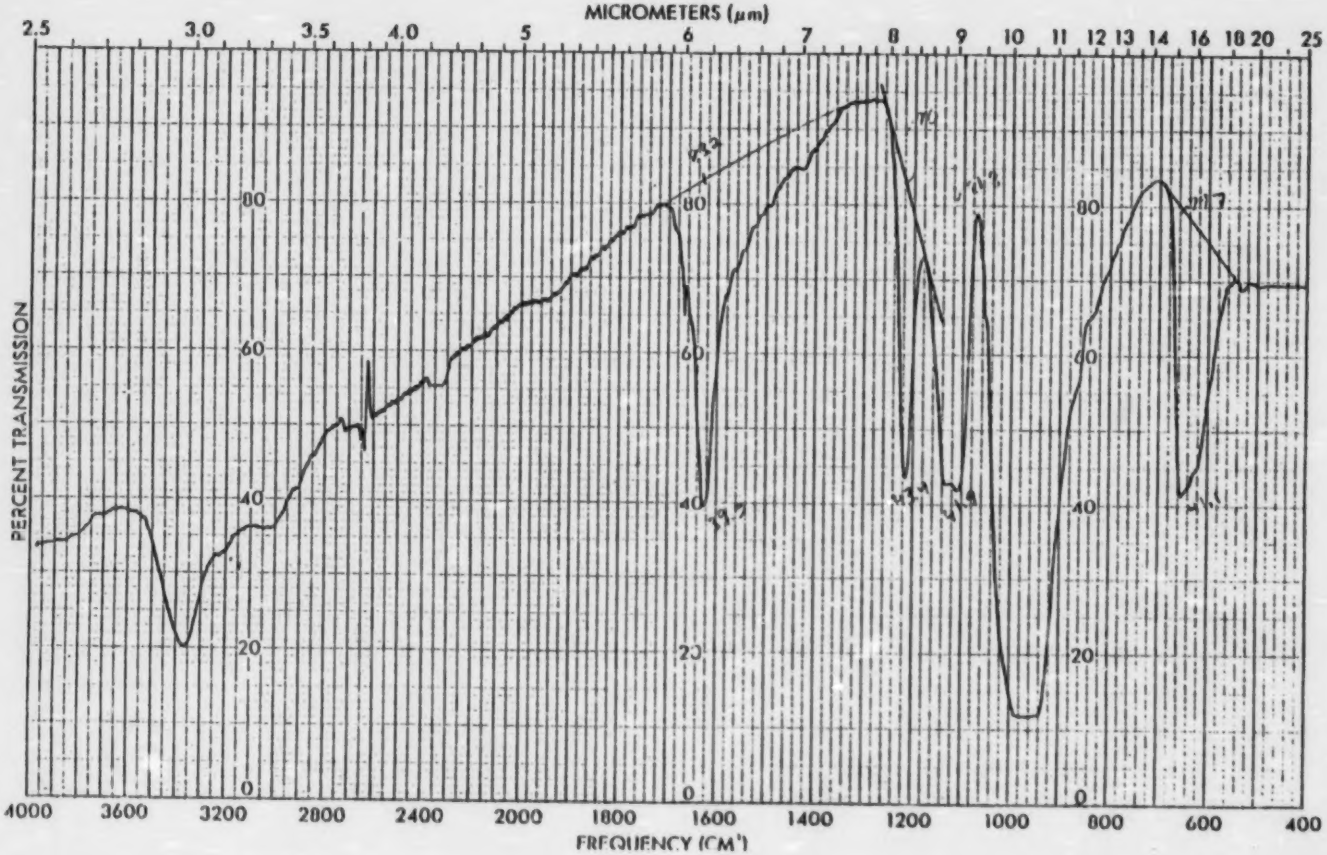


FIGURE F-45. INFRARED SPECTRA OF KINETIC RUN 44 PRECIPITATED SOLIDS

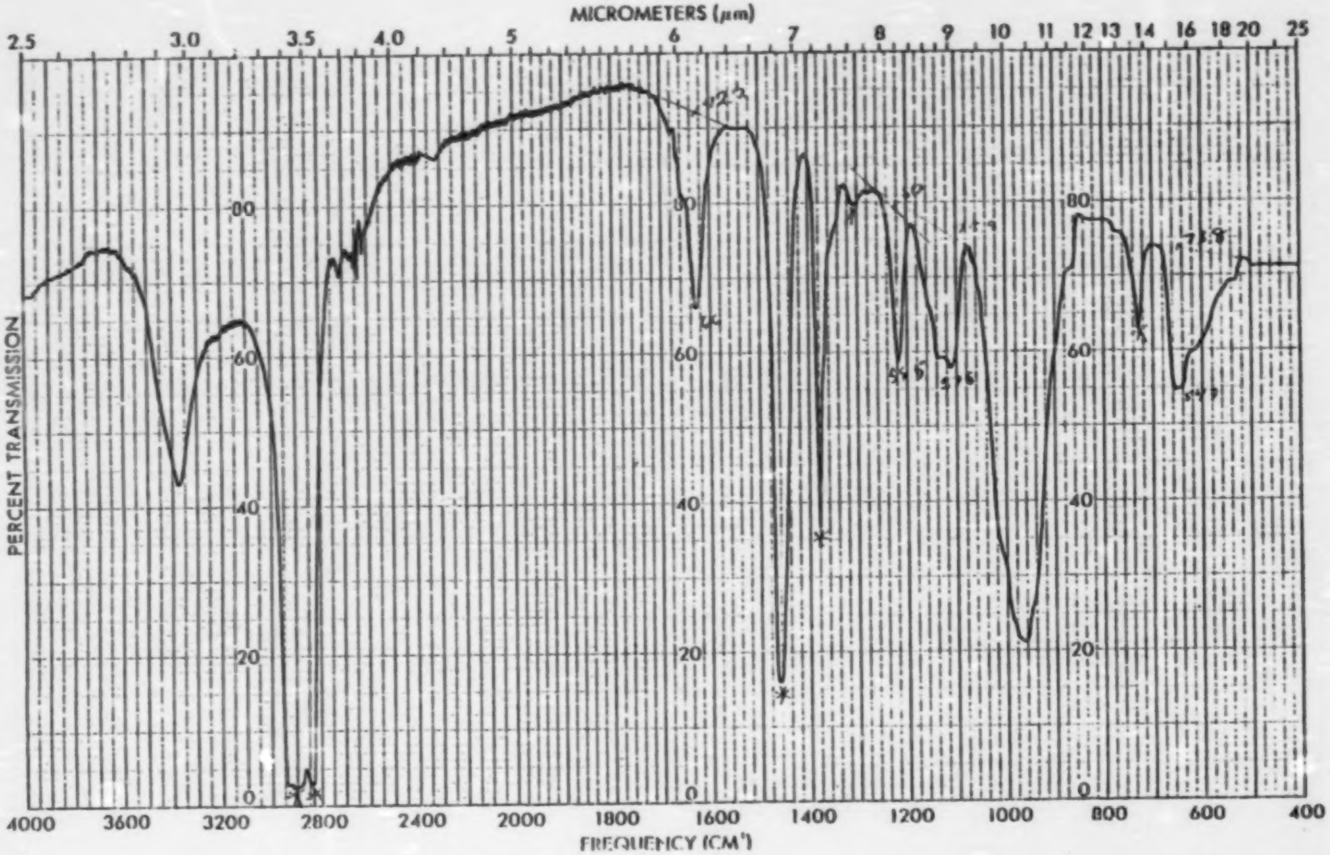


FIGURE F-46. INFRARED SPECTRA OF KINETIC RUN 44 PRECIPITATED SOLIDS

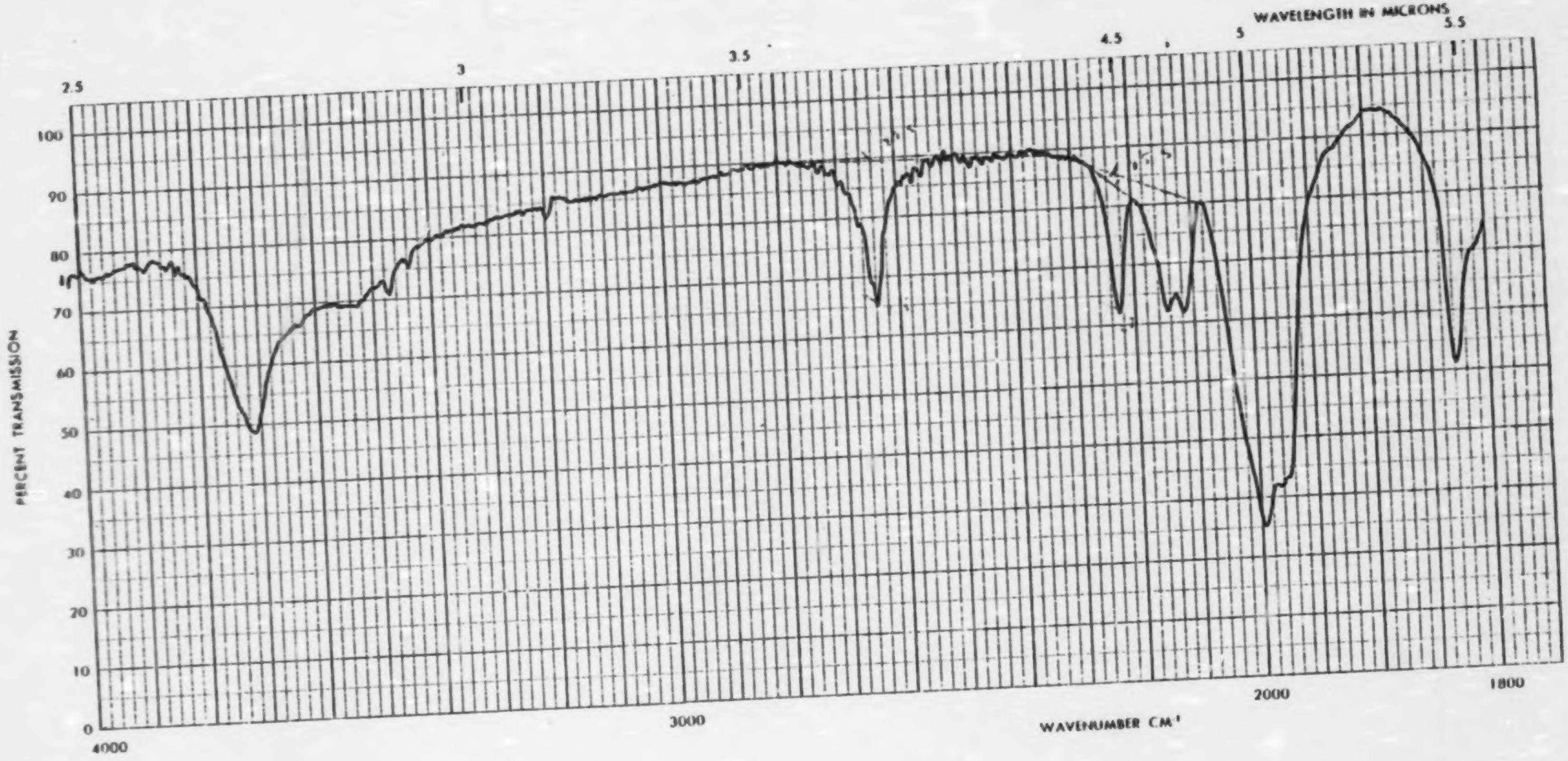


FIGURE F-47. INFRARED SPECTRA OF KINETIC RUN 46
PRECIPITATED SOLIDS

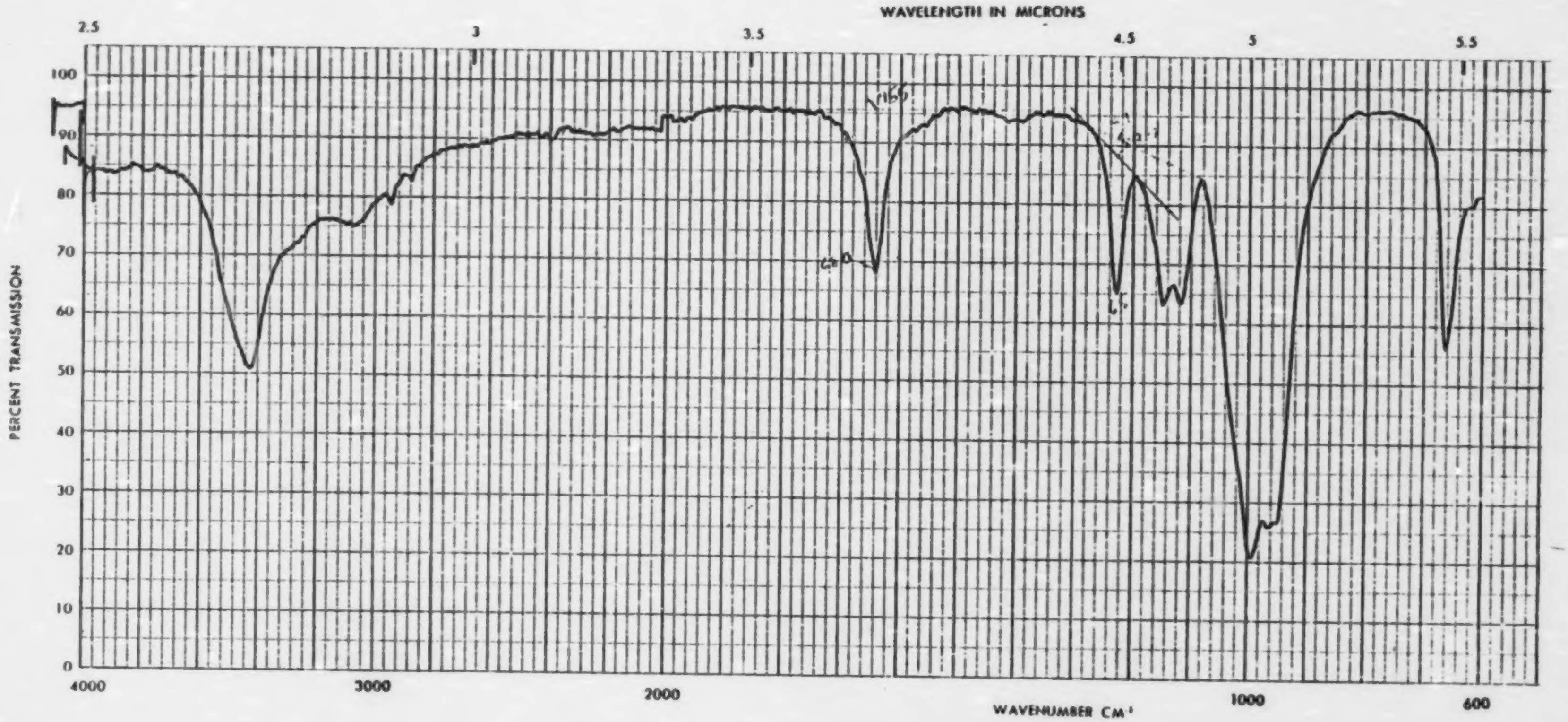


FIGURE F-48. INFRARED SPECTRA OF KINETIC RUN 47 PRECIPITATED SOLIDS

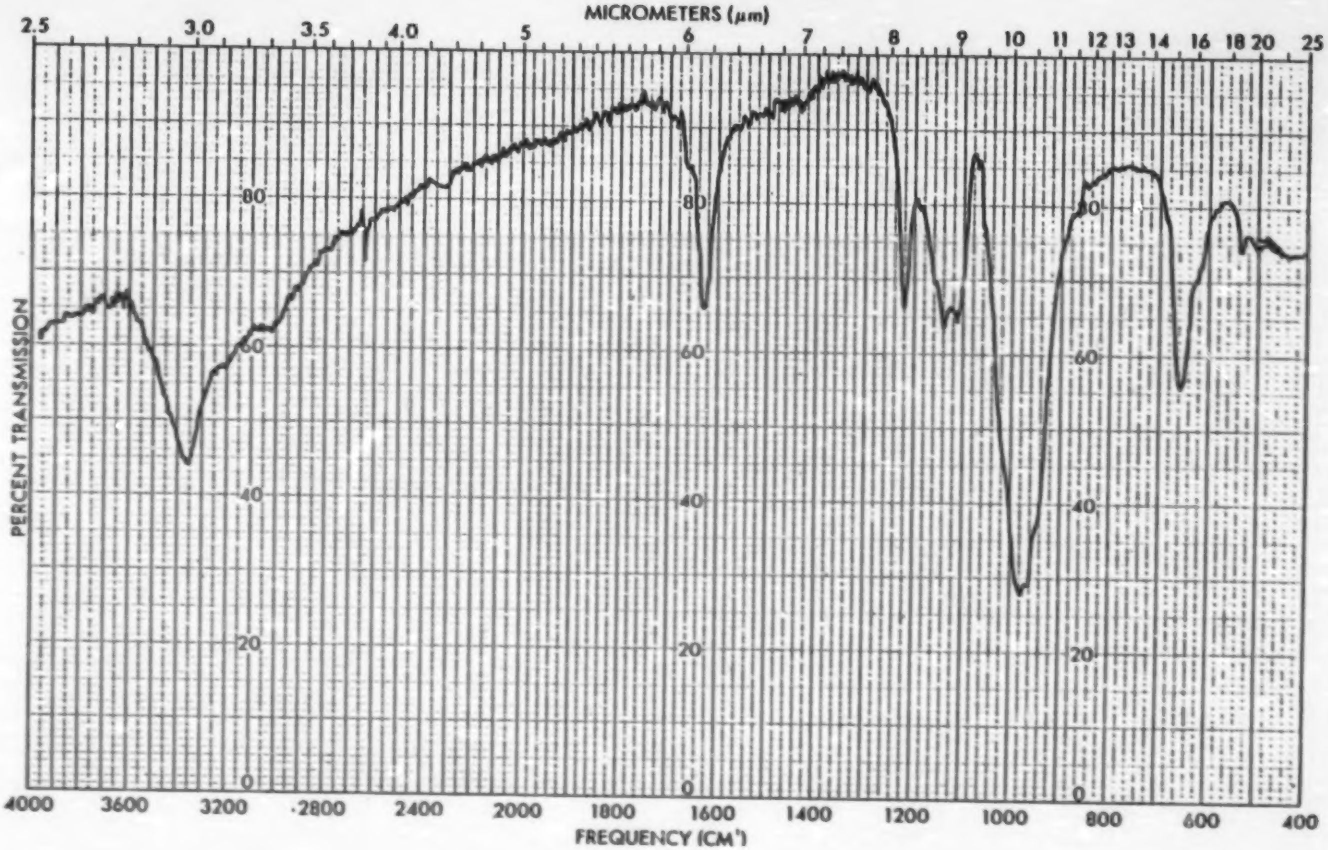


FIGURE F-49. INFRARED SPECTRA OF KINETIC RUN 48 PRECIPITATED SOLIDS

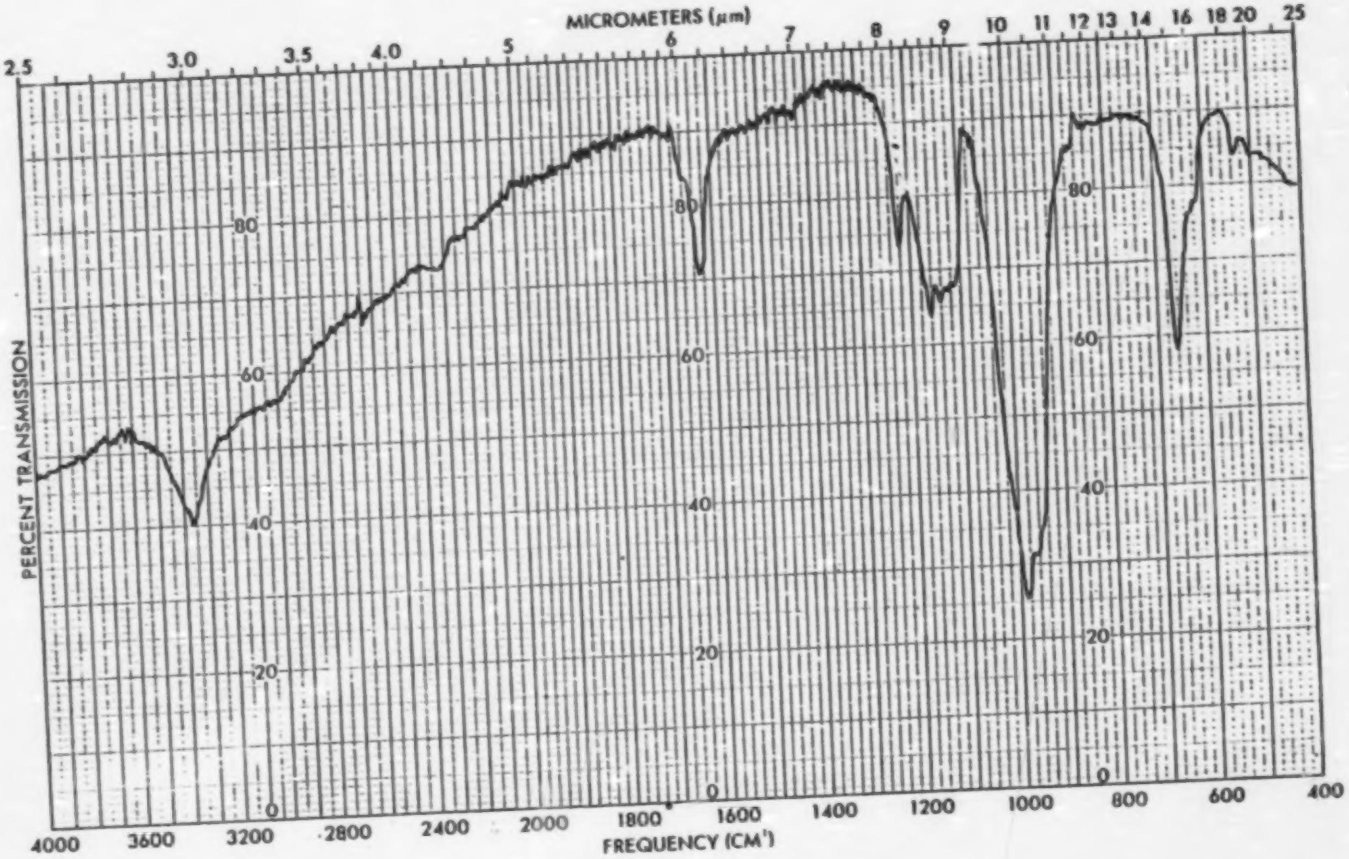


FIGURE F-50. INFRARED SPECTRA OF KINETIC RUN 49
PRECIPITATED SOLIDS

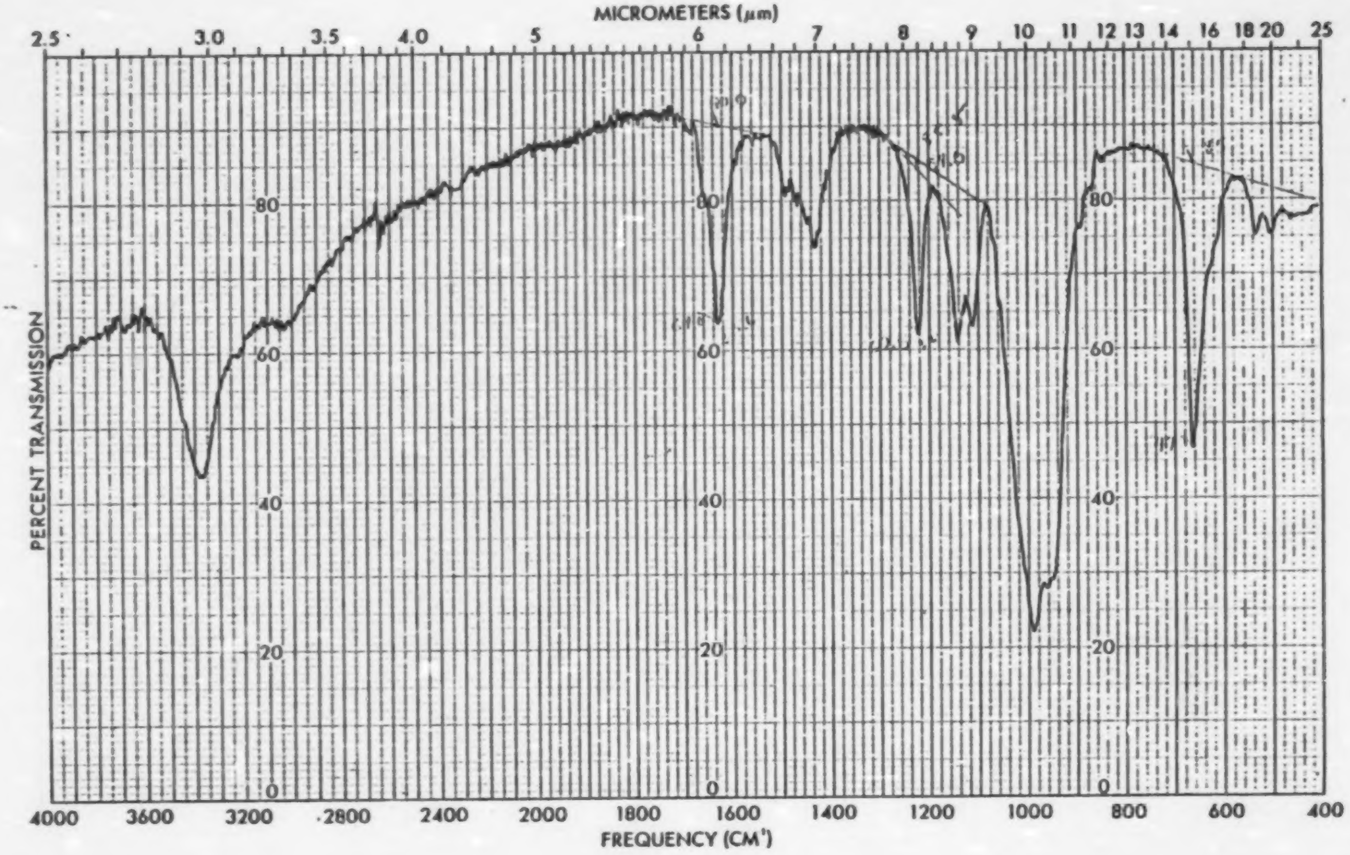


FIGURE F-51. INFRARED SPECTRA OF KINETIC RUN 53 PRECIPITATED SOLIDS

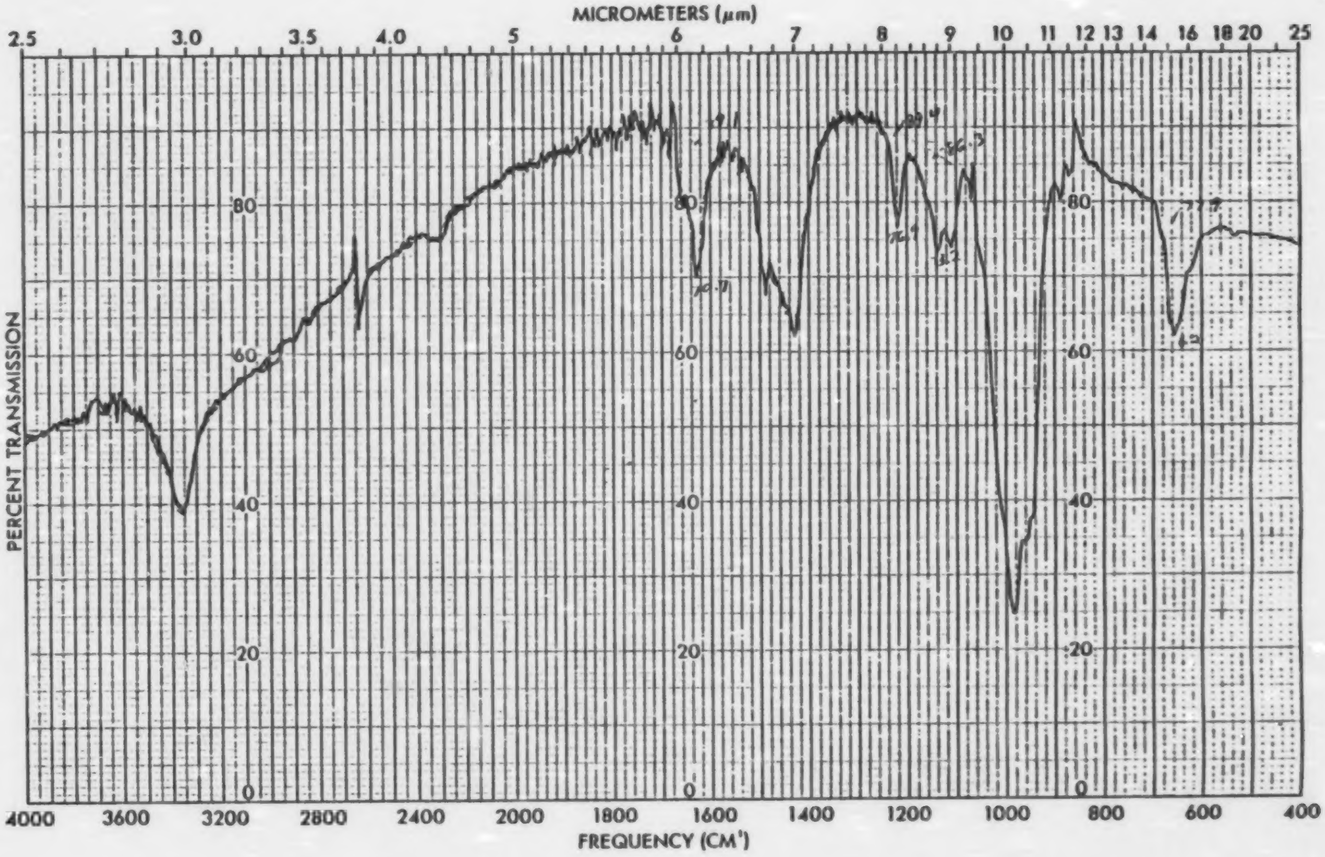


FIGURE F-52. INFRARED SPECTRA OF KINETIC RUN 60 PRECIPITATED SOLIDS

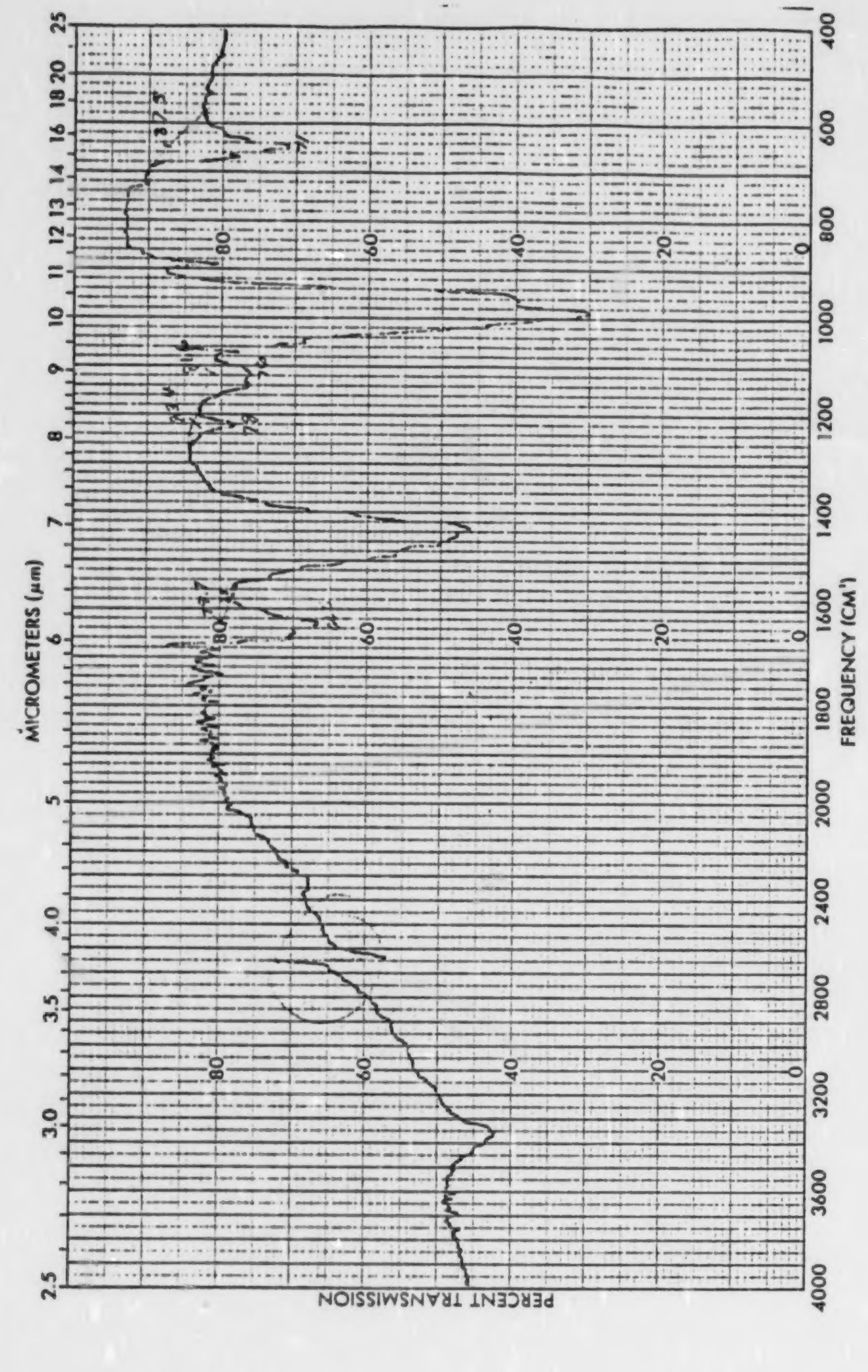


FIGURE F-53. INFRARED SPECTRA OF KINETIC RUN 61 PRECIPITATED SOLIDS

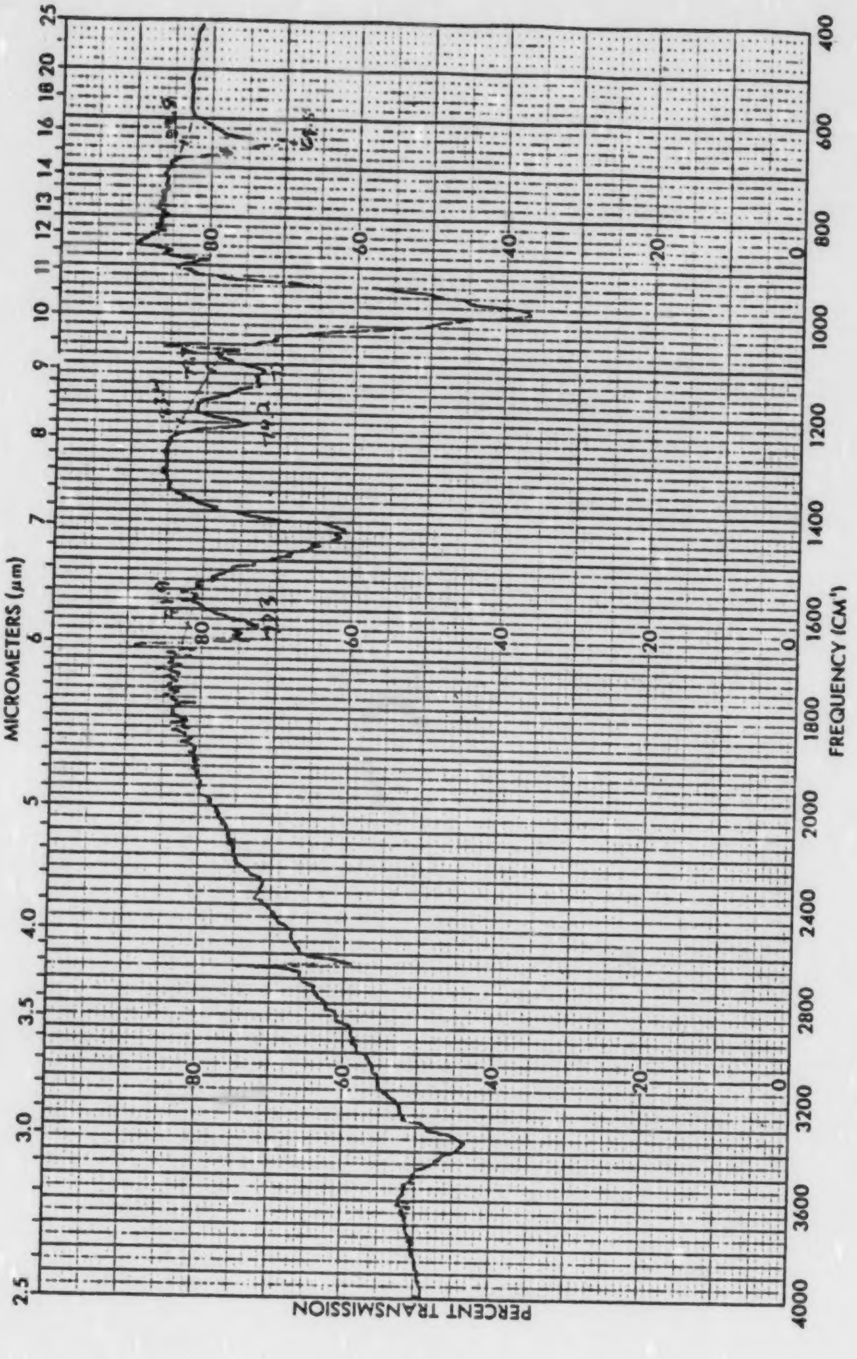


FIGURE F-54. INFRARED SPECTRA OF KINETIC RUN 62 PRECIPITATED SOLIDS

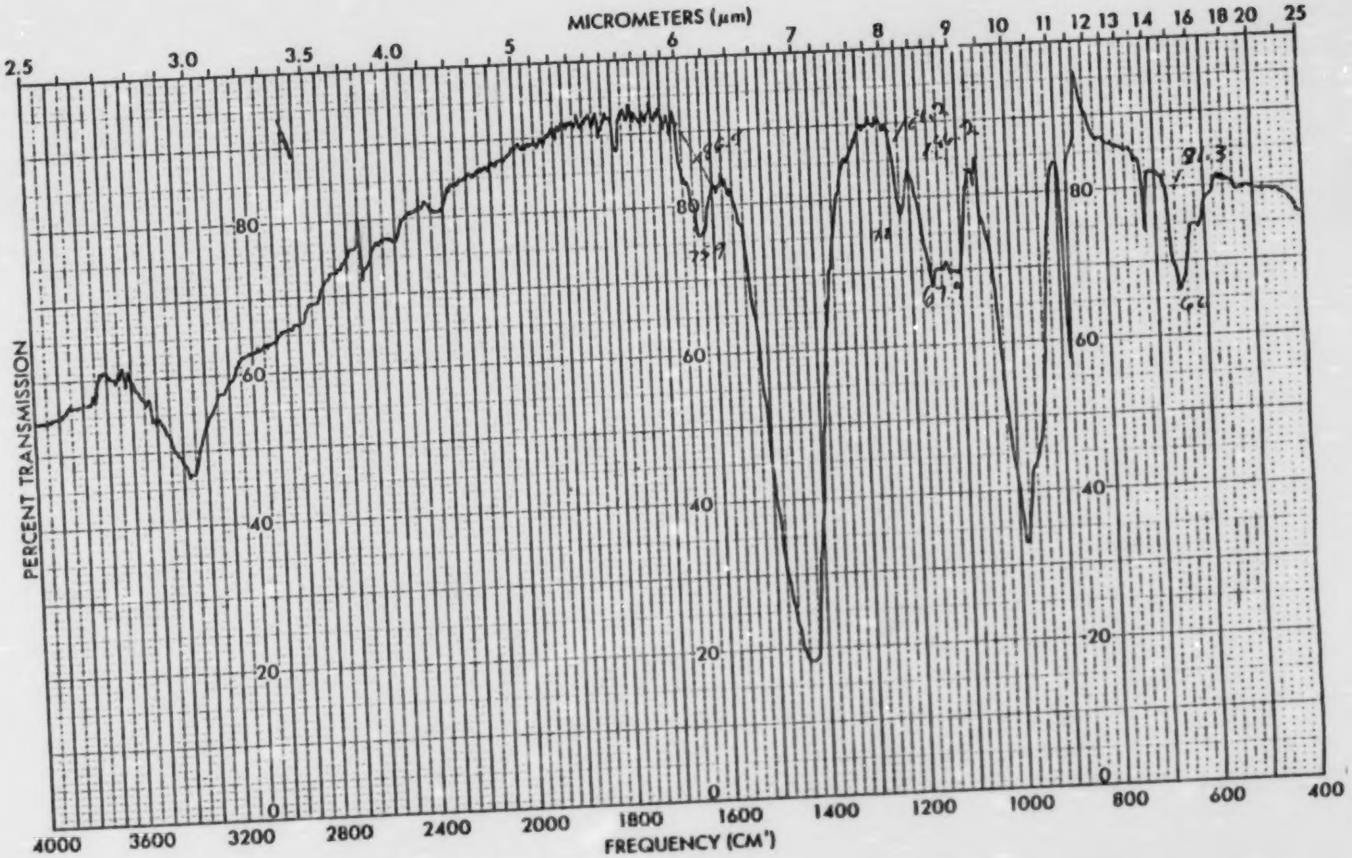


FIGURE F-55. INFRARED SPECTRA OF KINETIC RUN 63 PRECIPITATED SOLIDS

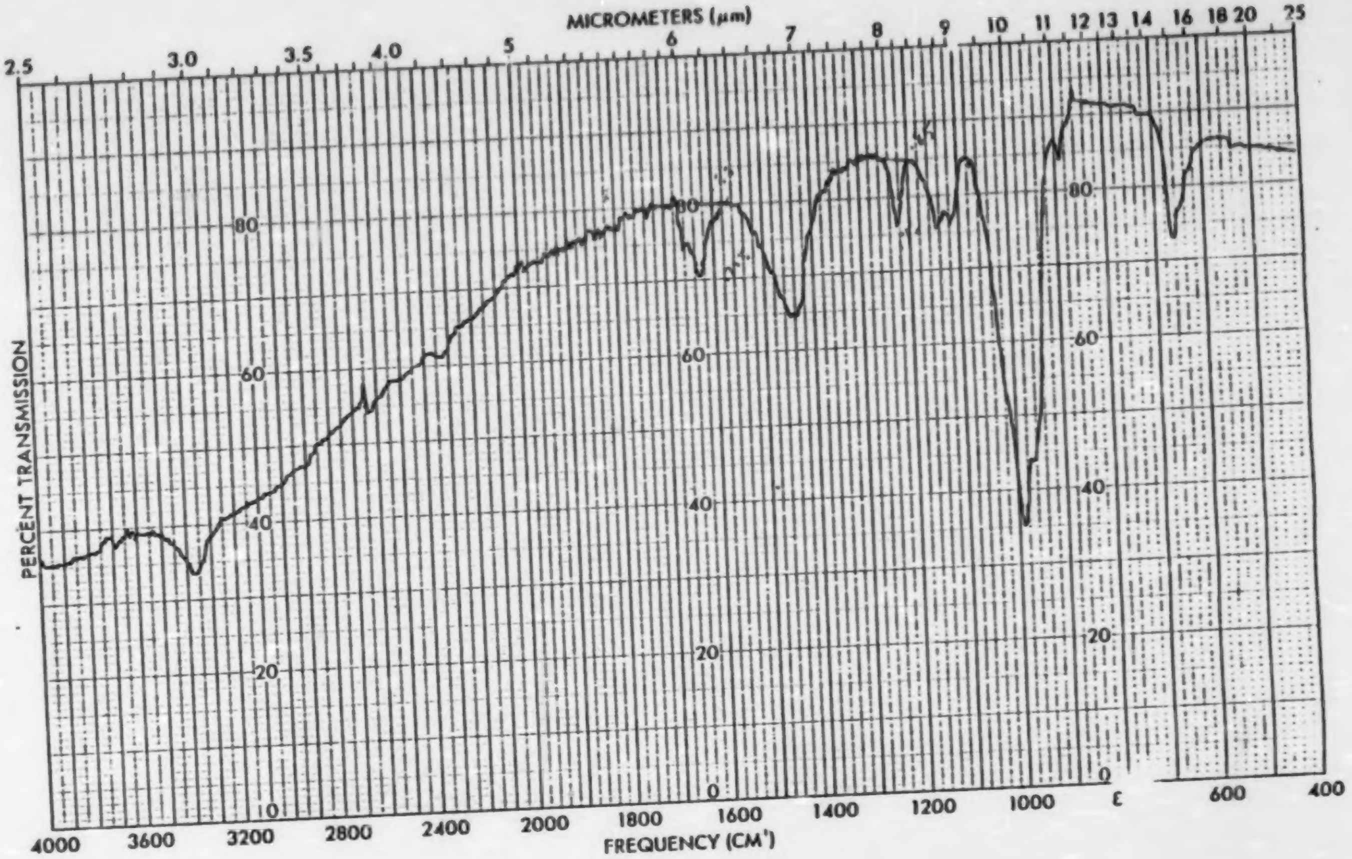


FIGURE F-56. INFRARED SPECTRA OF KINETIC RUN 63-B PRECIPITATED SOLIDS

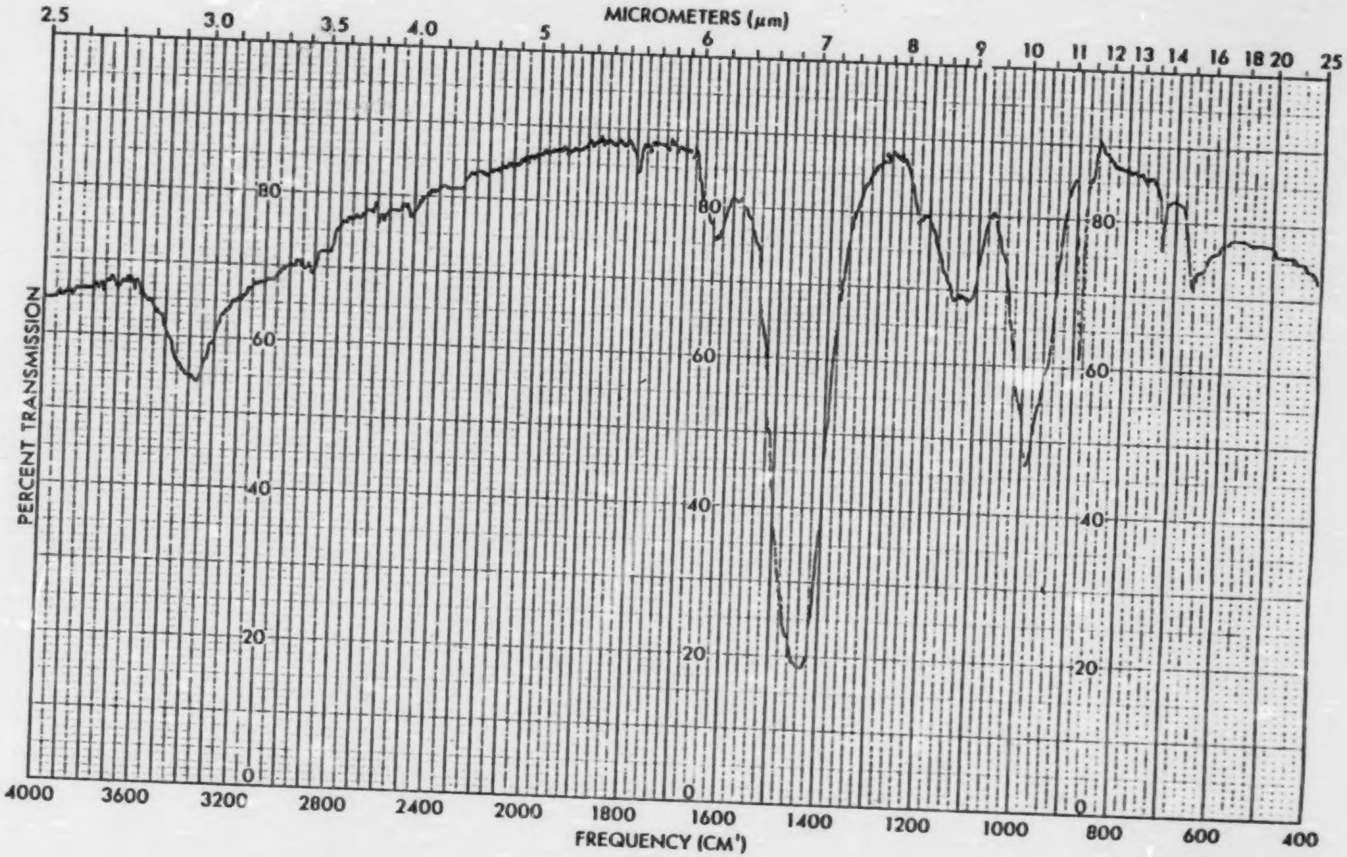


FIGURE F-57. INFRARED SPECTRA OF KINETIC RUN 64
PRECIPITATED SOLIDS

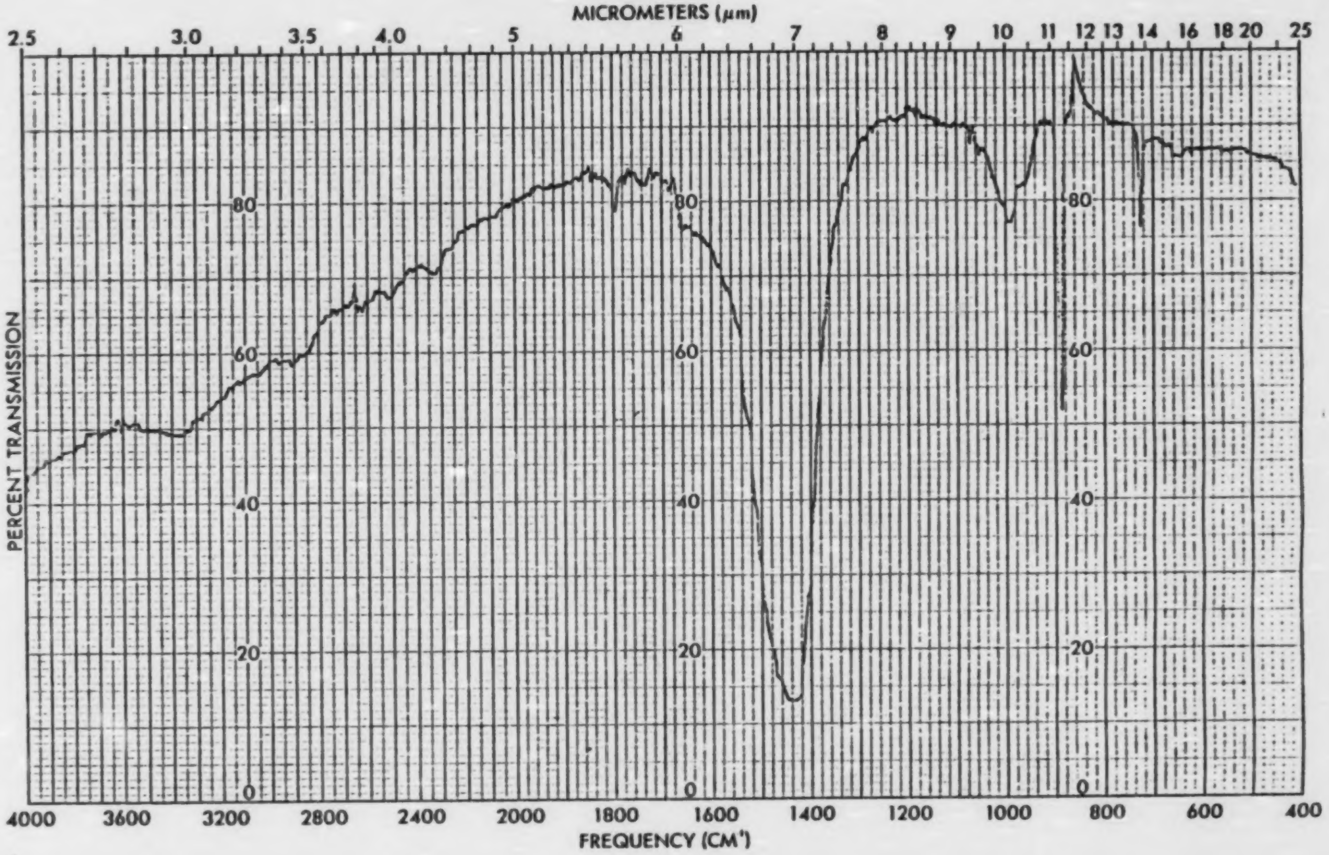


FIGURE F-58. INFRARED SPECTRA OF KINETIC RUN 65
PRECIPITATED SOLIDS

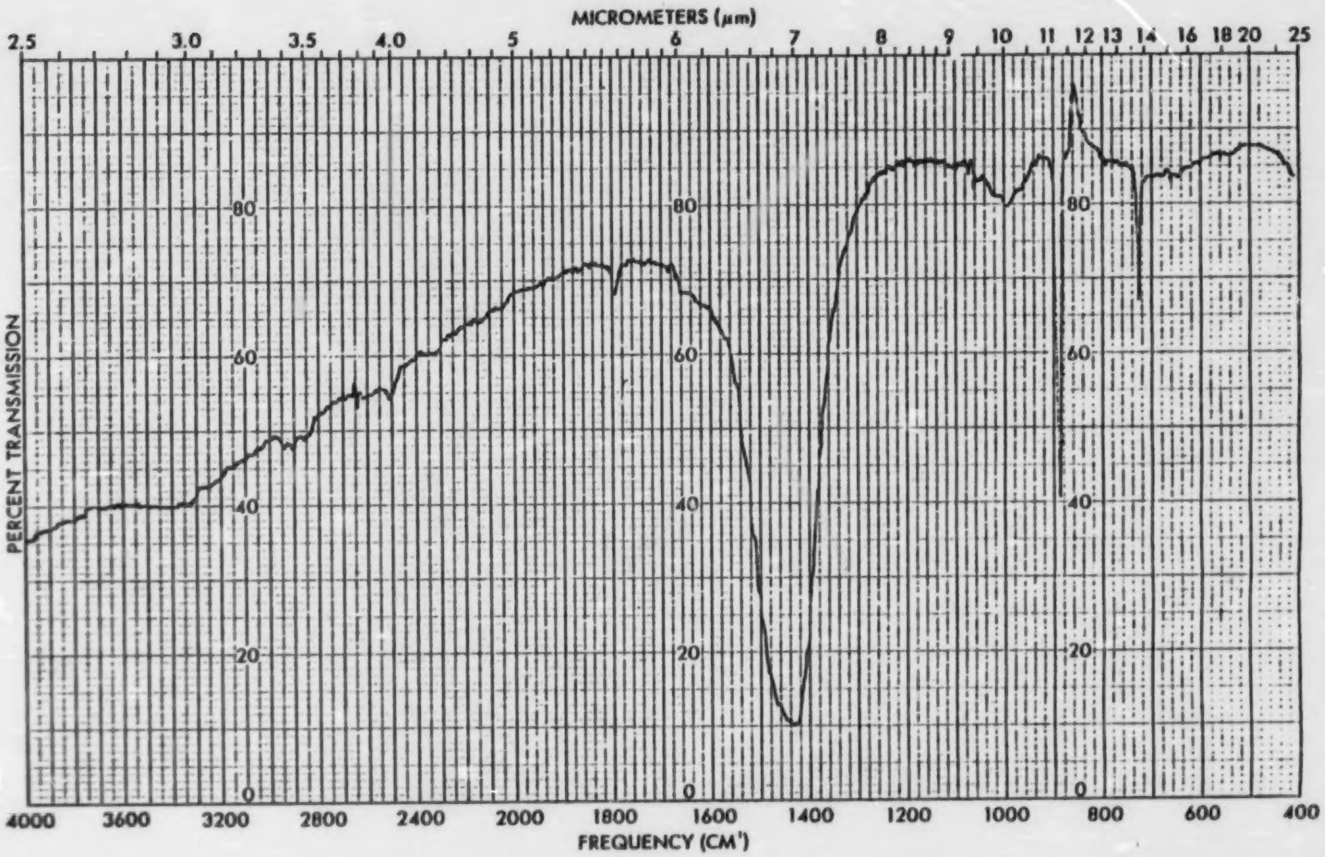


FIGURE F-59. INFRARED SPECTRA OF KINETIC RUN 66 PRECIPITATED SOLIDS

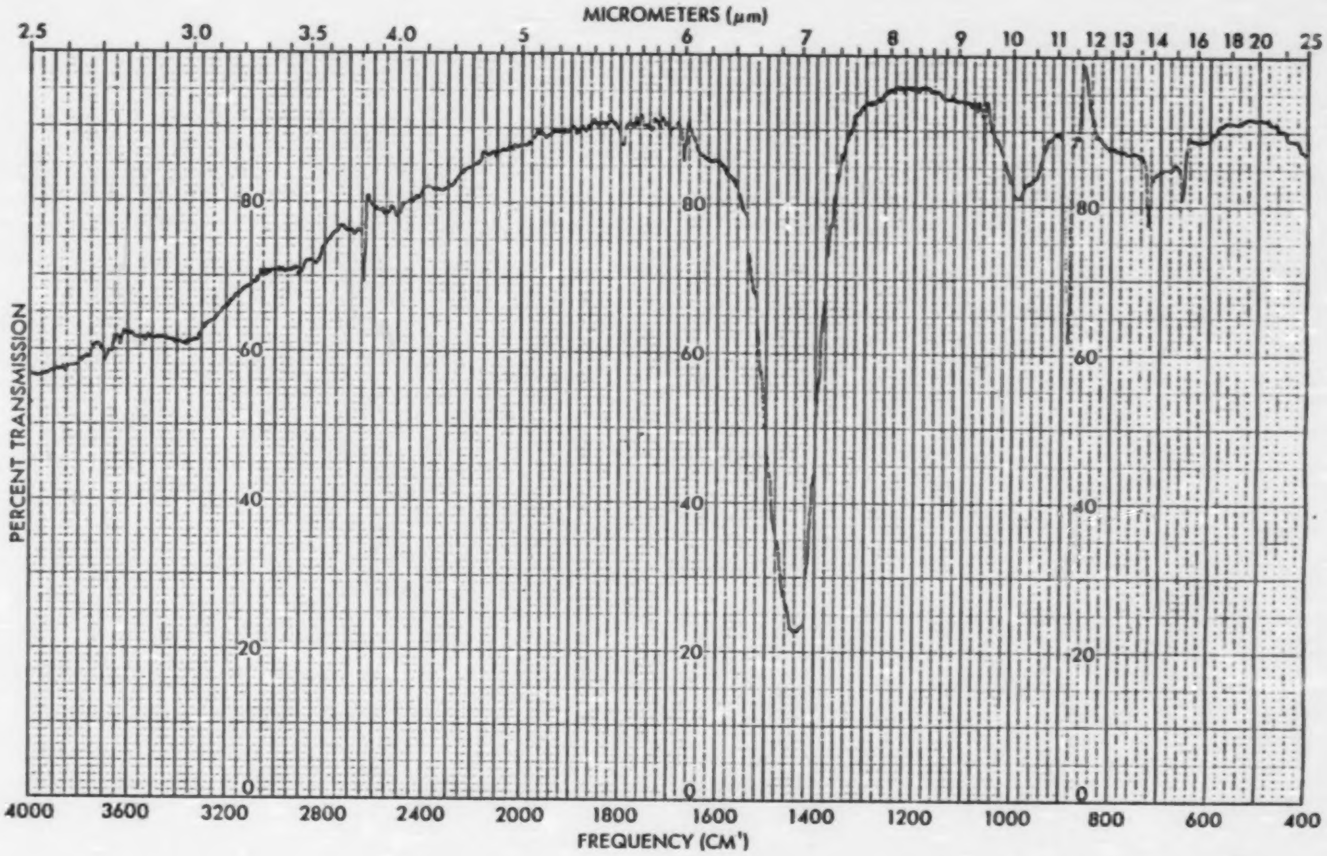


FIGURE F-60. INFRARED SPECTRA OF KINETIC RUN 67 PRECIPITATED SOLIDS

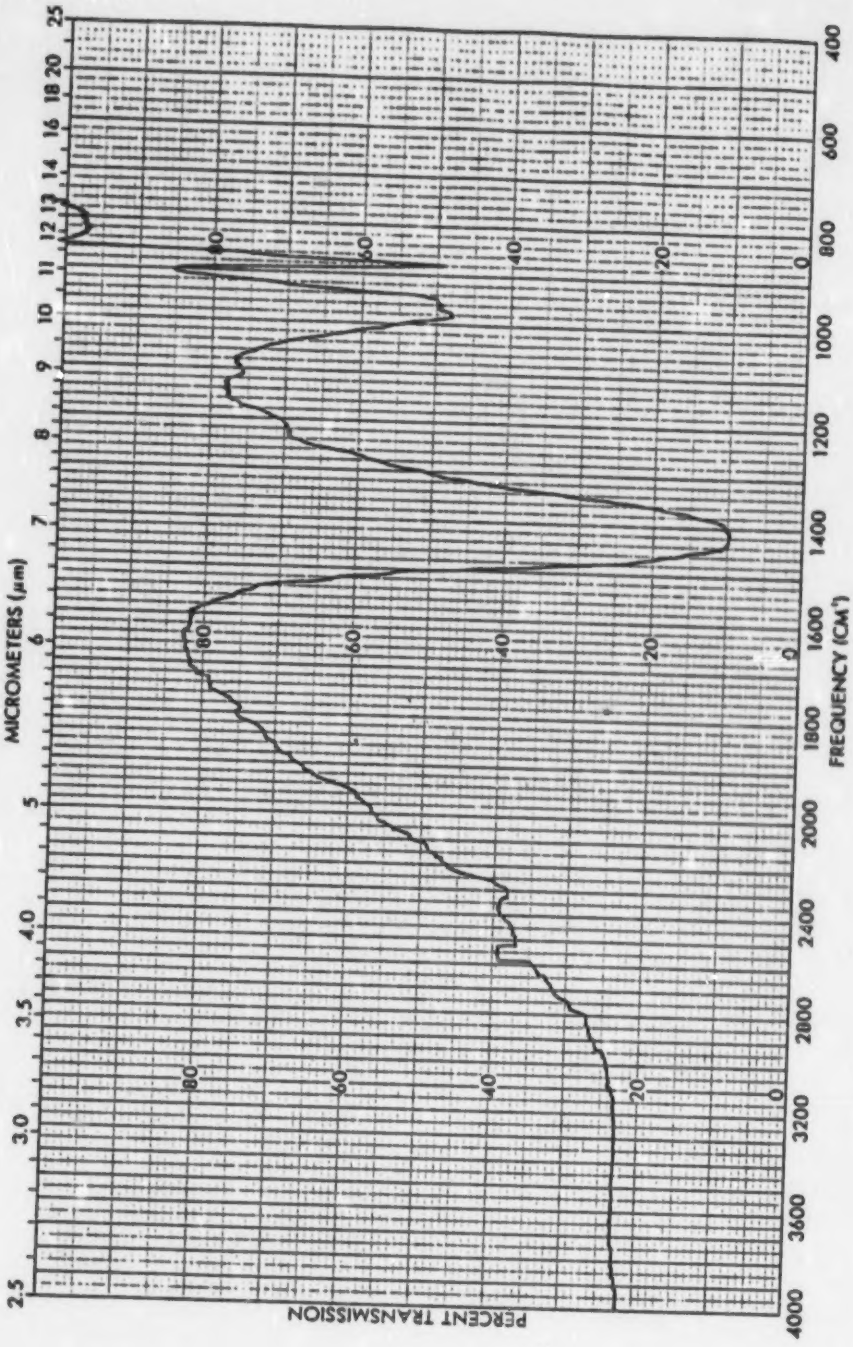


FIGURE F-61. INFRARED SPECTRA OF KINETIC RUN 68
PRECIPITATED SOLIDS

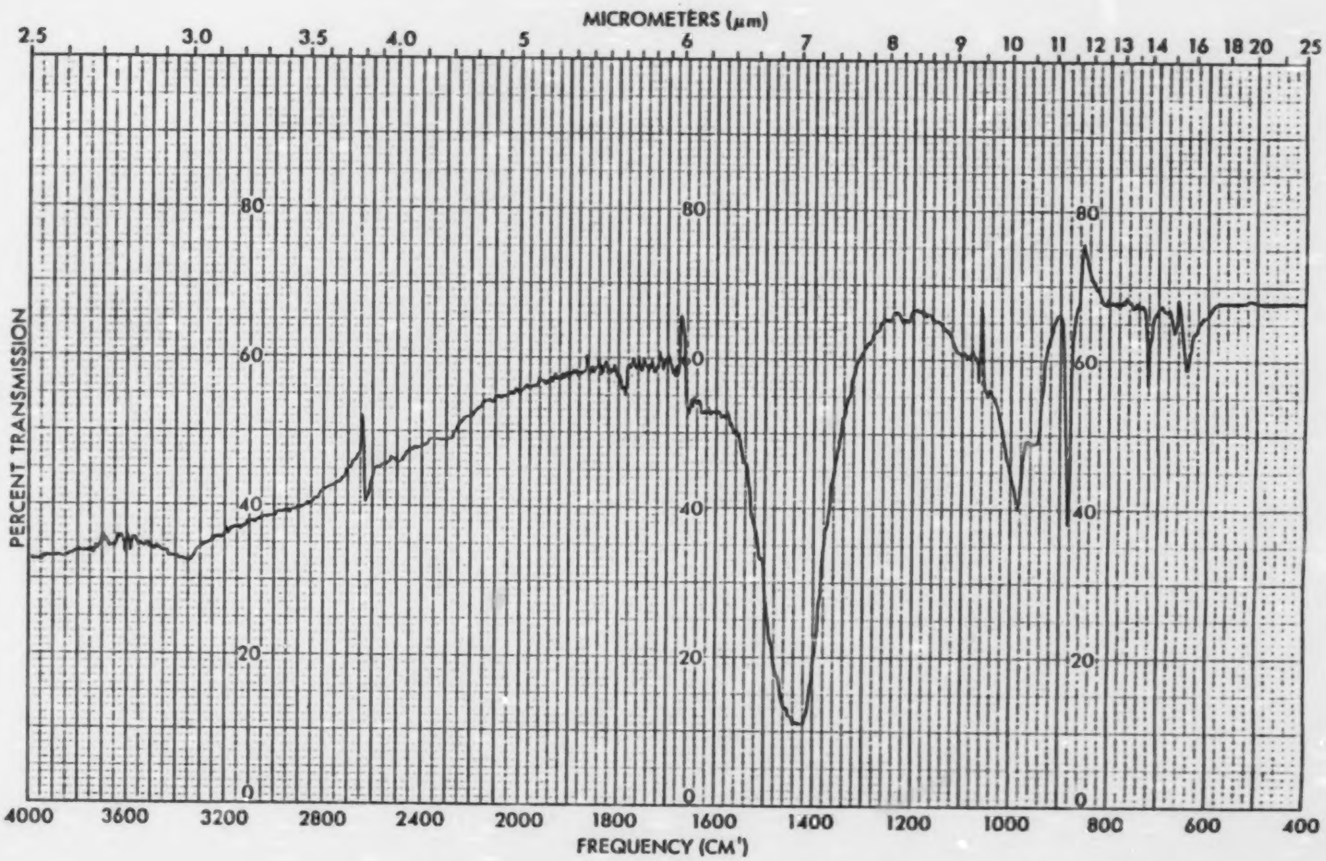


FIGURE F-62. INFRARED SPECTRA OF KINETIC RUN 68
PRECIPITATED SOLIDS

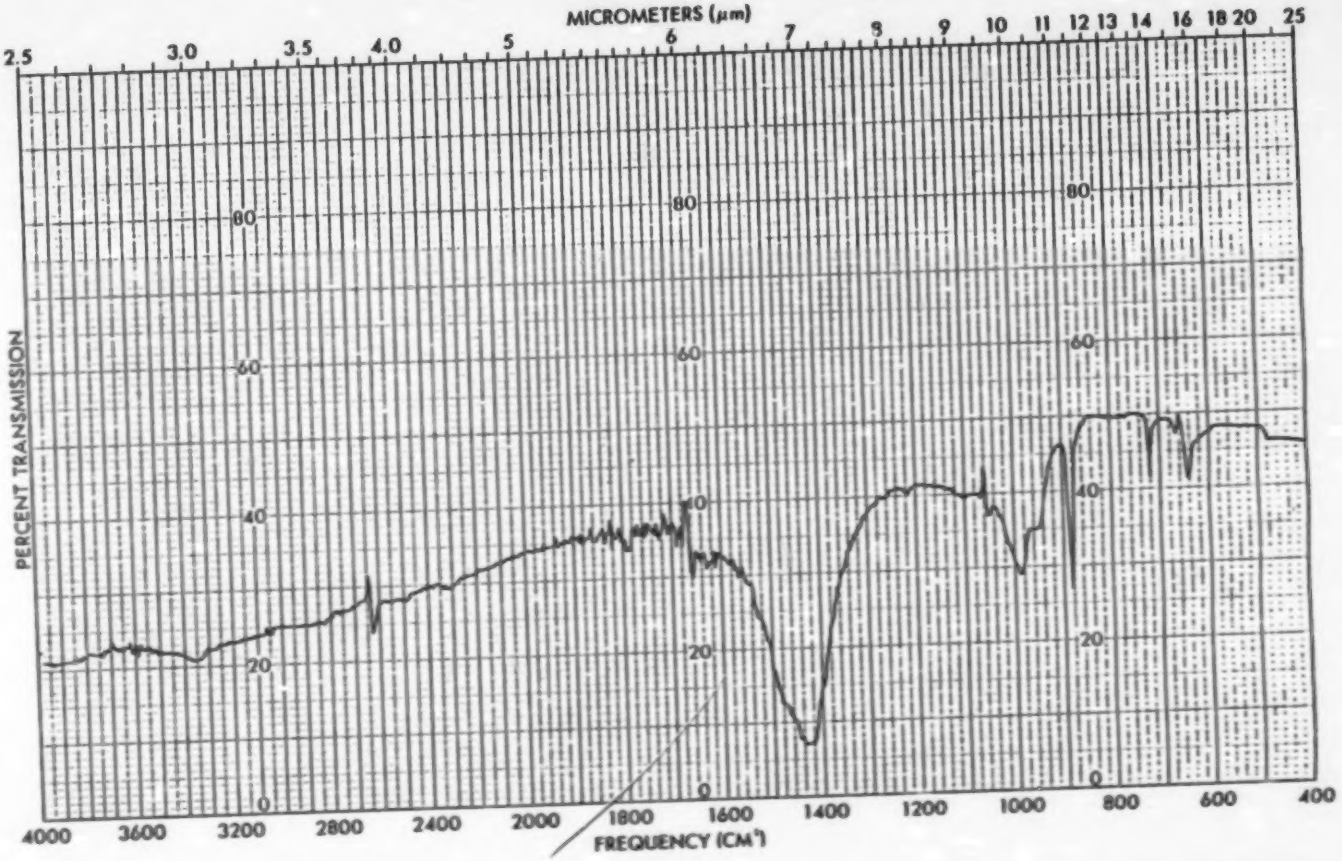


FIGURE F-63. INFRARED SPECTRA OF KINETIC RUN 68 PRECIPITATED SOLIDS

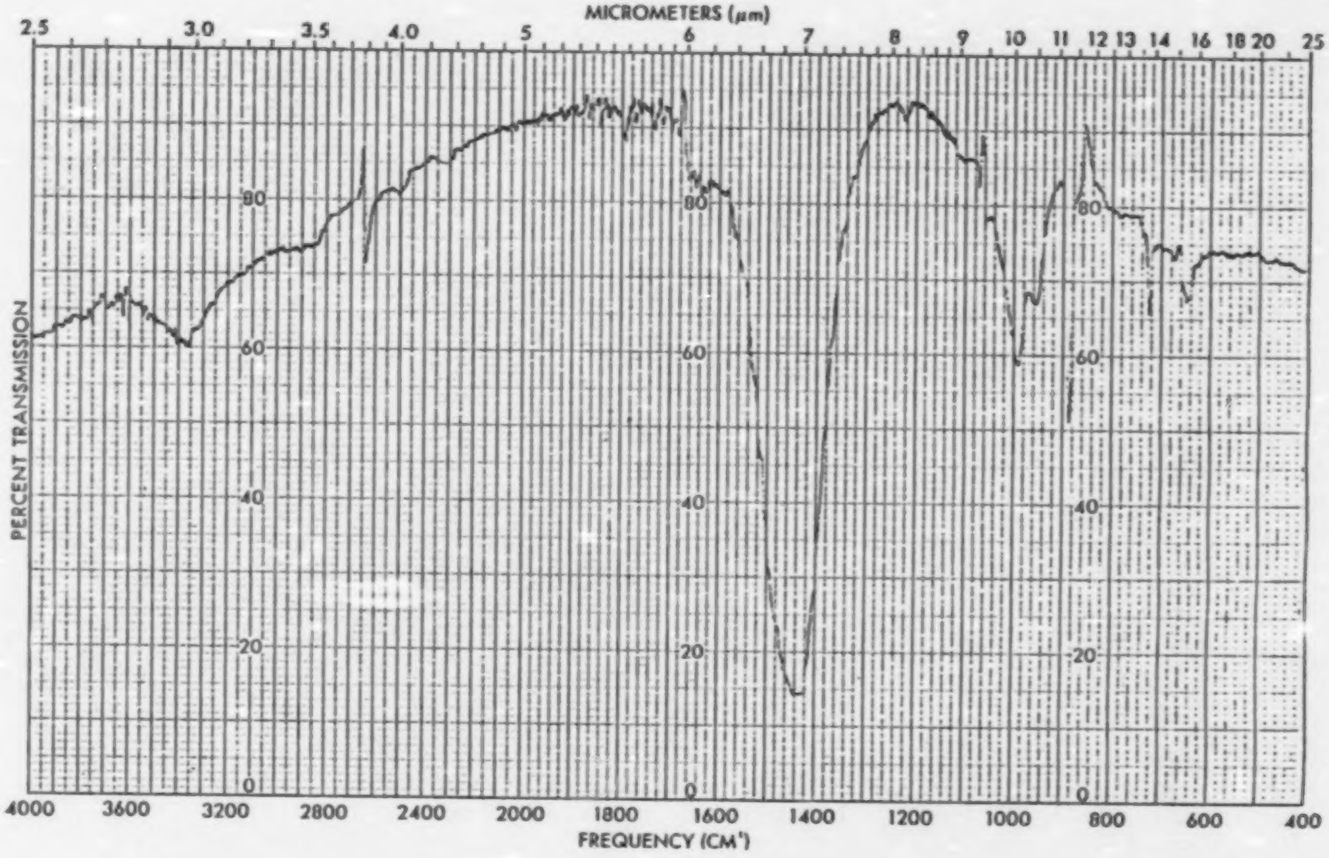


FIGURE F-64. INFRARED SPECTRA OF KINETIC RUN 68 PRECIPITATED SOLIDS

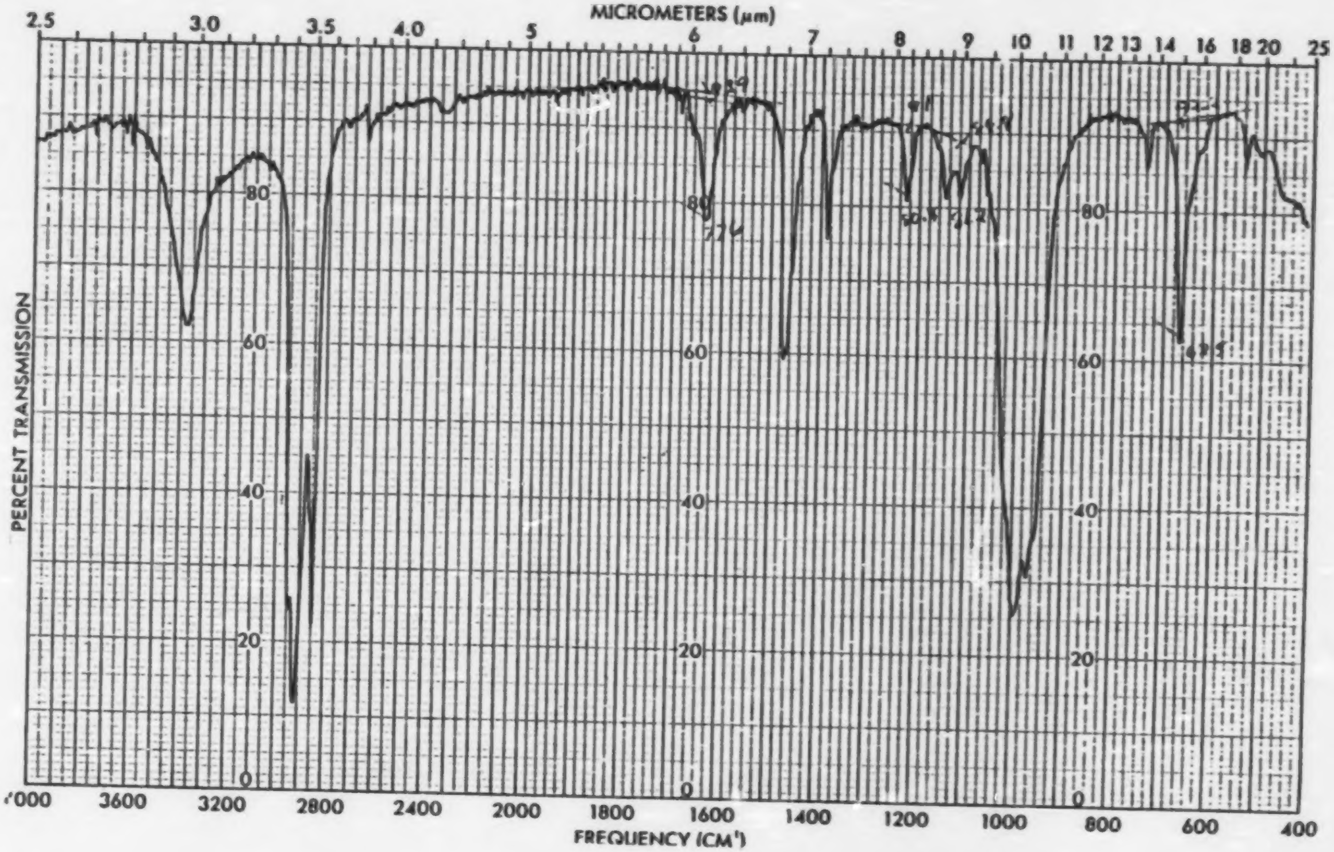


FIGURE F-65. INFRARED SPECTRA OF KINETIC RUN 69 PRECIPITATED SOLIDS

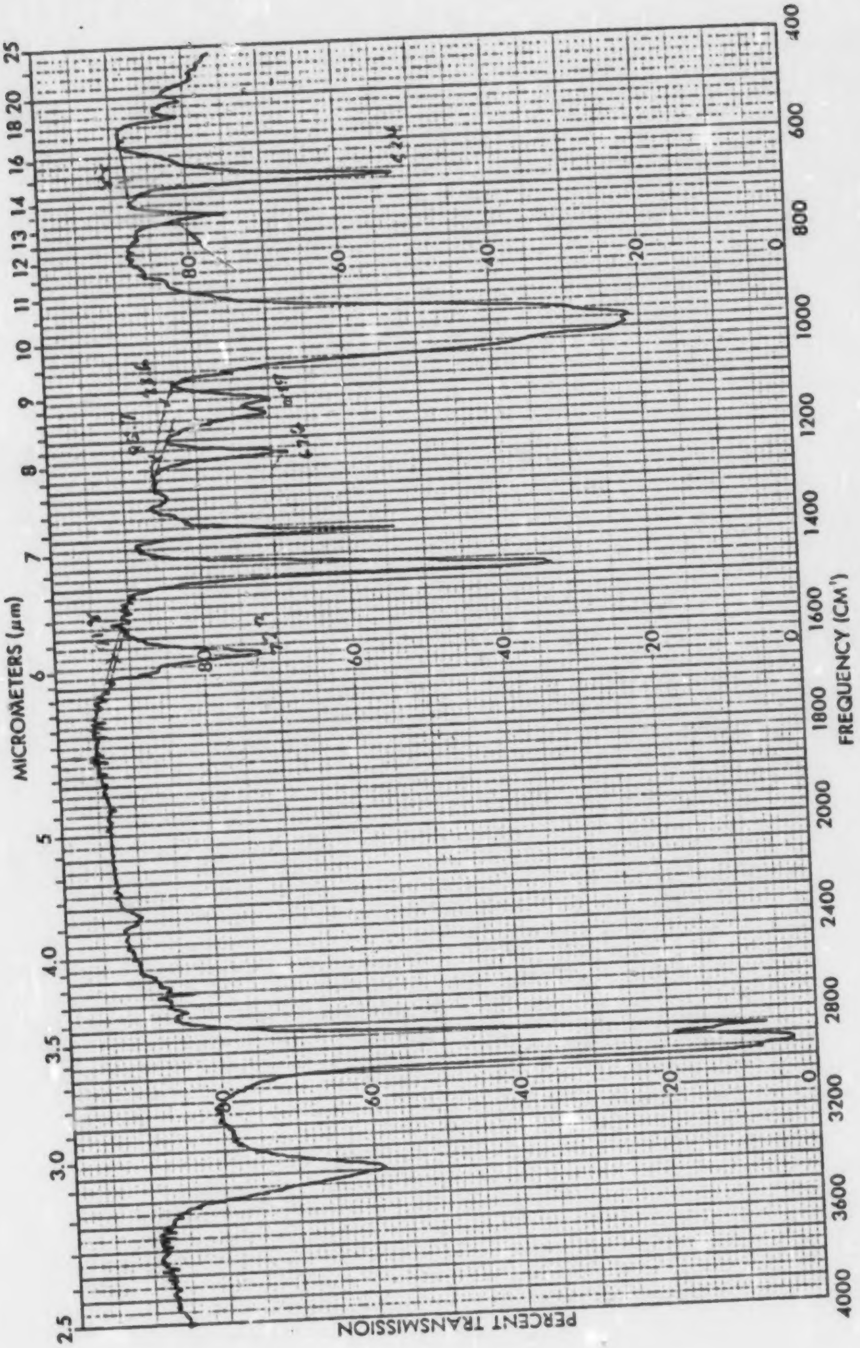


FIGURE F-66. INFRARED SPECTRA OF KINETIC RUN 70 PRECIPITATED SOLIDS

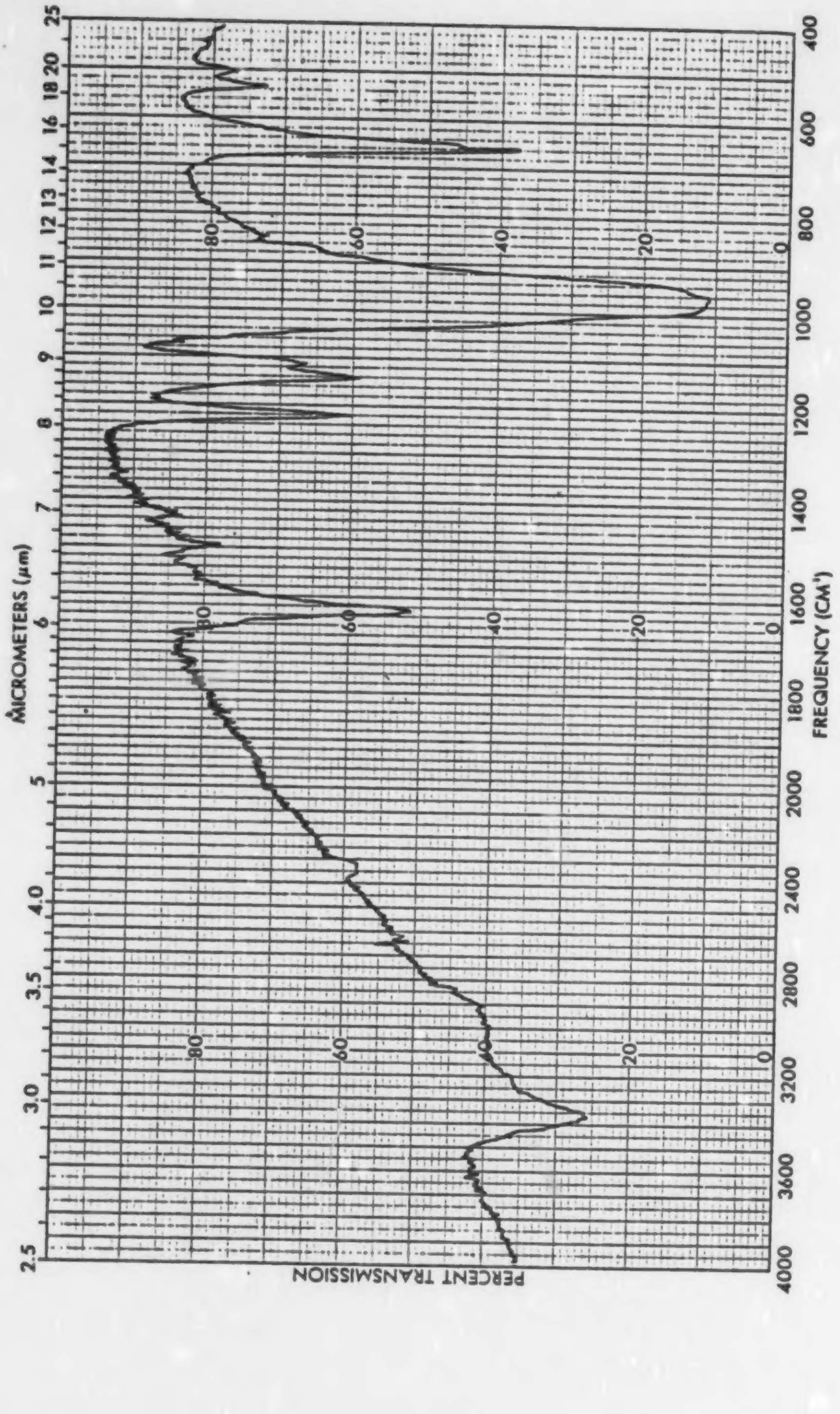


FIGURE F-67. INFRARED SPECTRA OF KINETIC RUN 71 PRECIPITATED SOLIDS

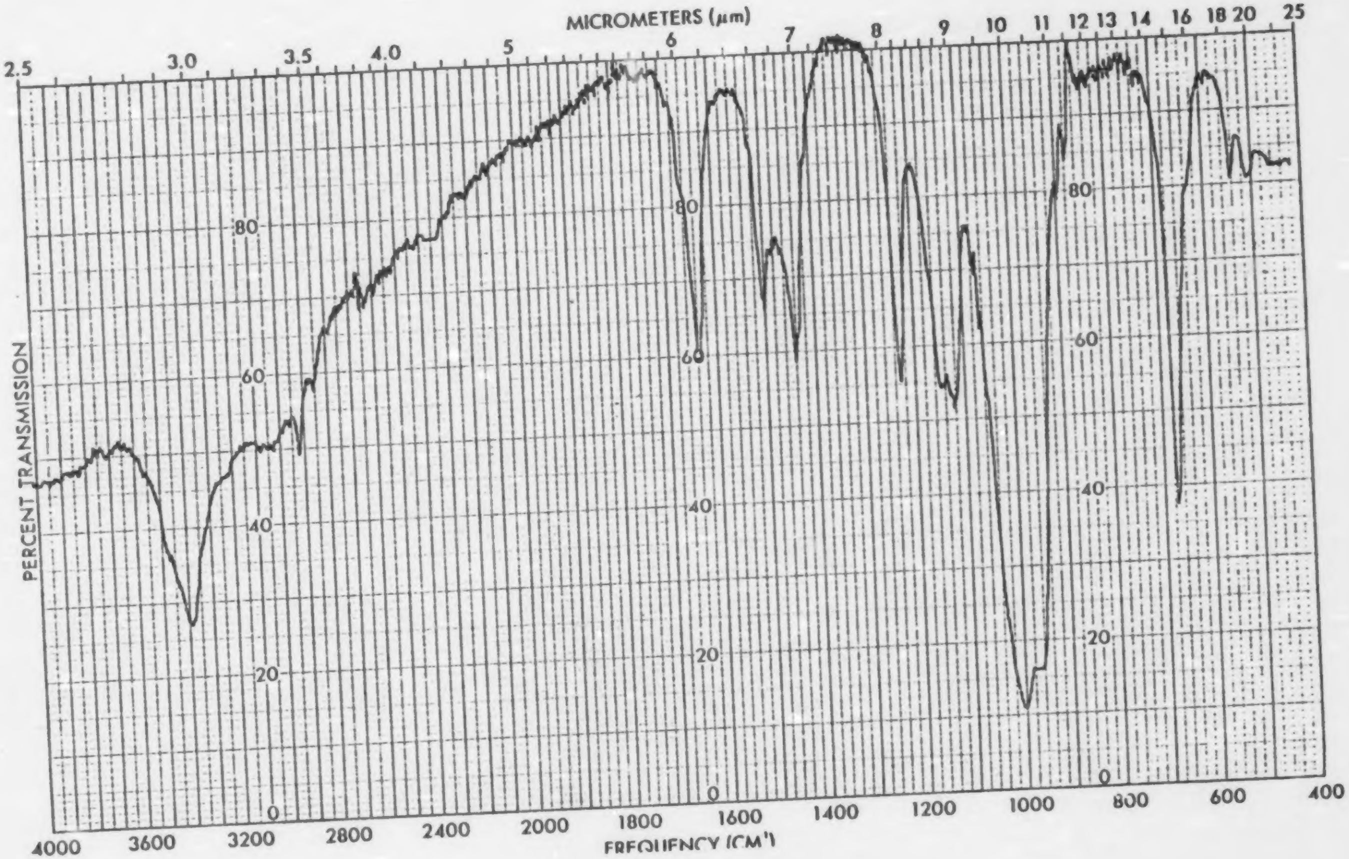


FIGURE F-68. INFRARED SPECTRA OF PP&L SCRUBBER SOLIDS FROM RUN 66

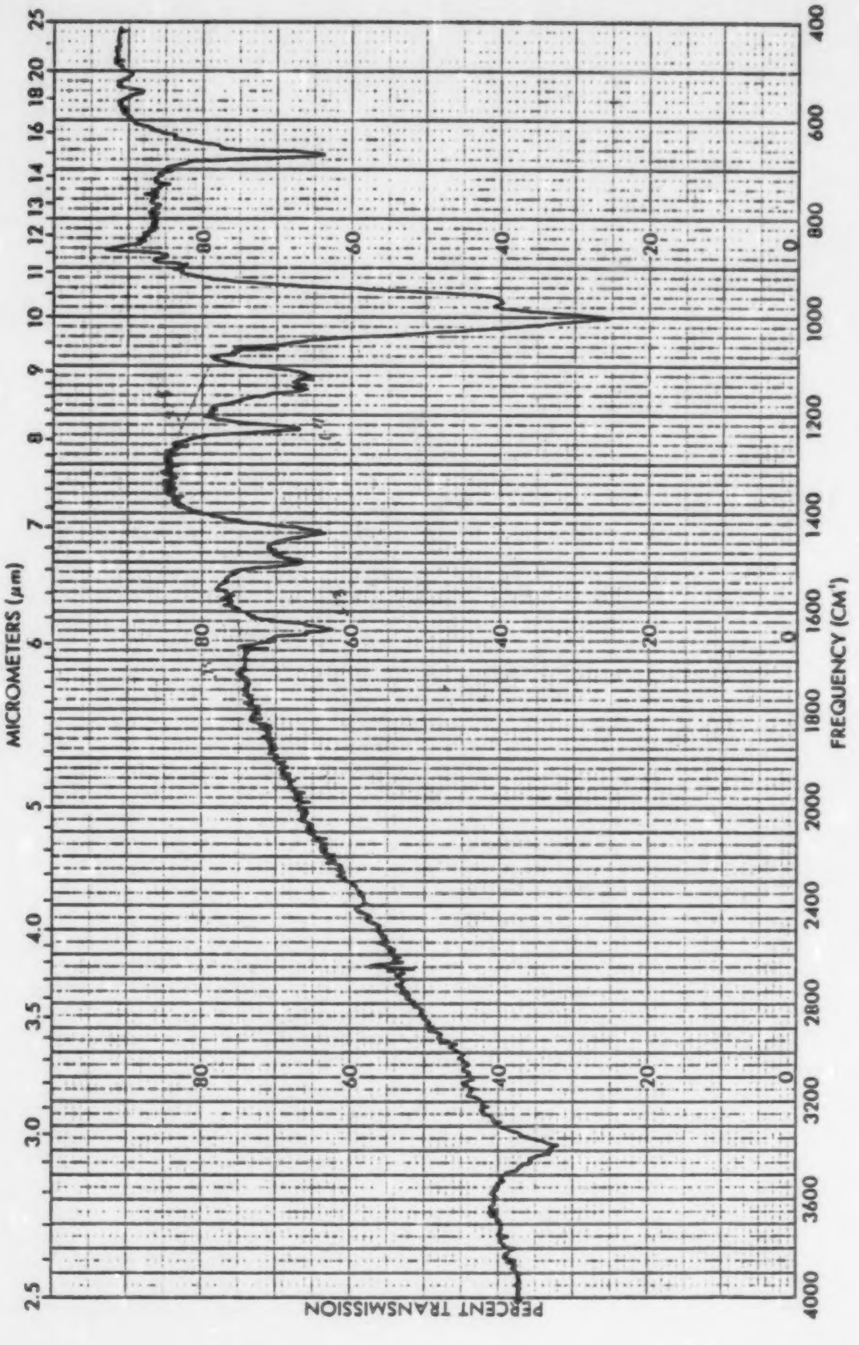


FIGURE F-69. INFRARED SPECTRA OF PP&L SCRUBBER SOLIDS FROM RUN 67

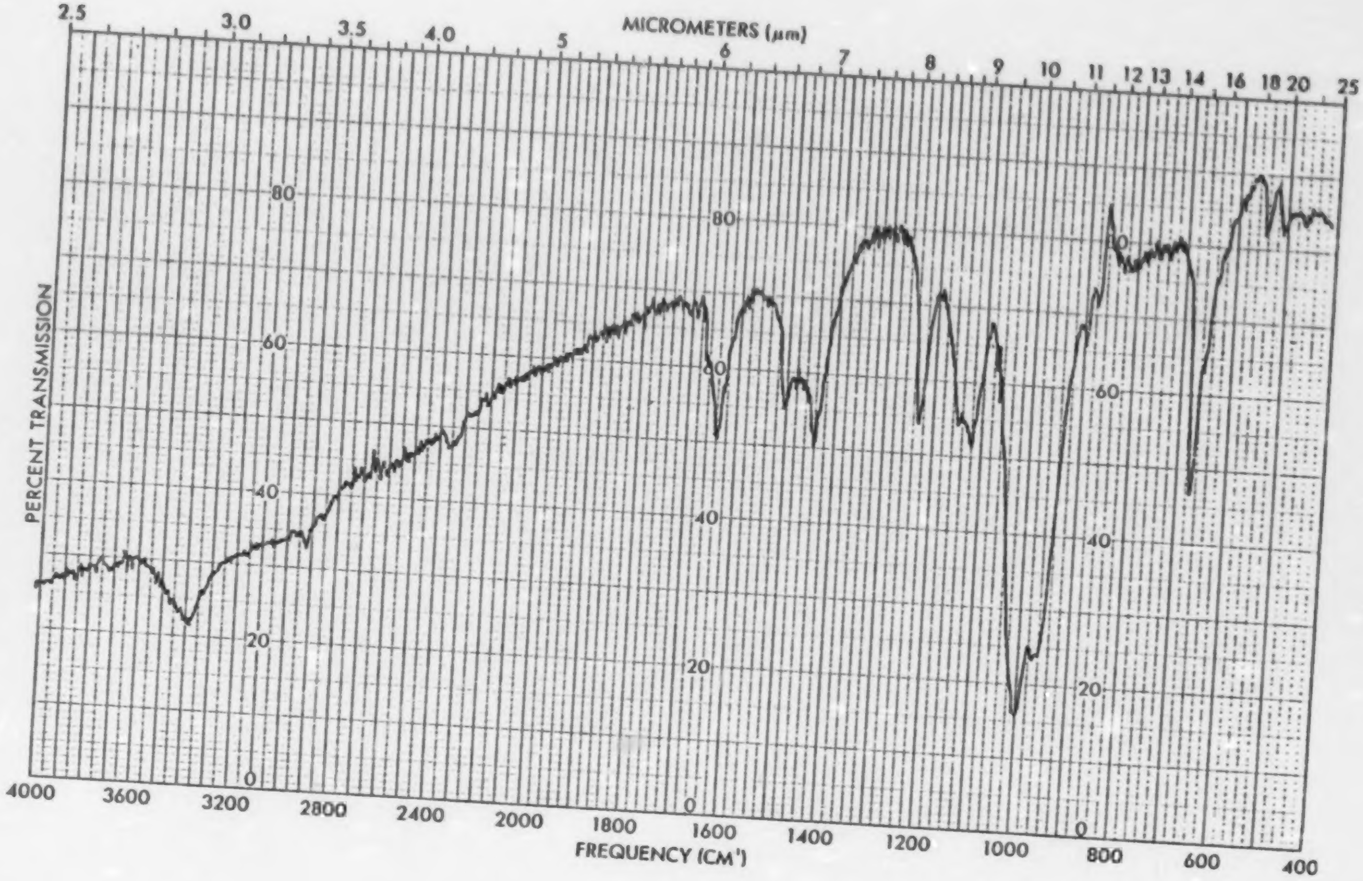


FIGURE F-70. INFRARED SPECTRA OF PP&L SCRUBBER SOLIDS FROM RUN 67

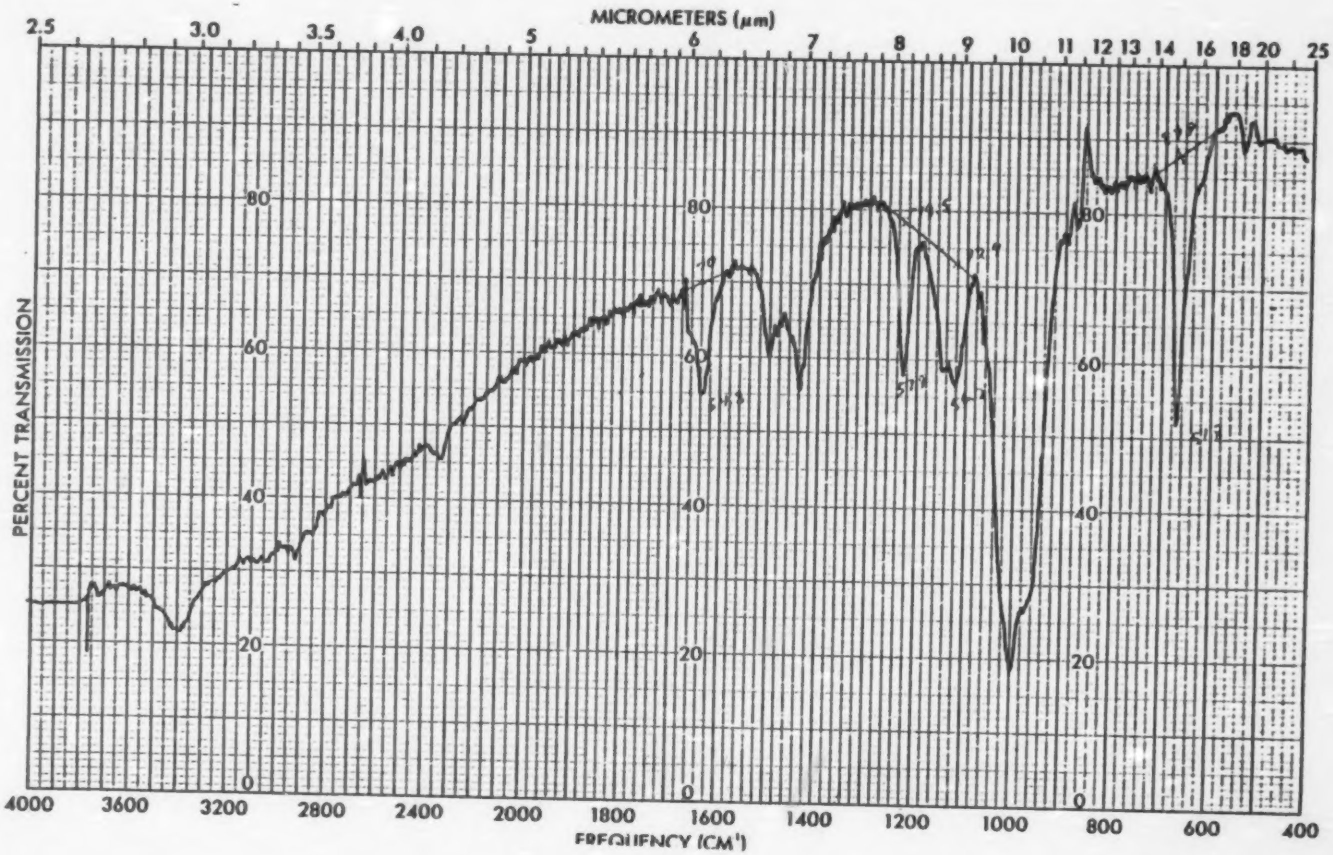


FIGURE F-71. INFRARED SPECTRA OF PP&L SCRUBBER SOLIDS FROM RUN 67

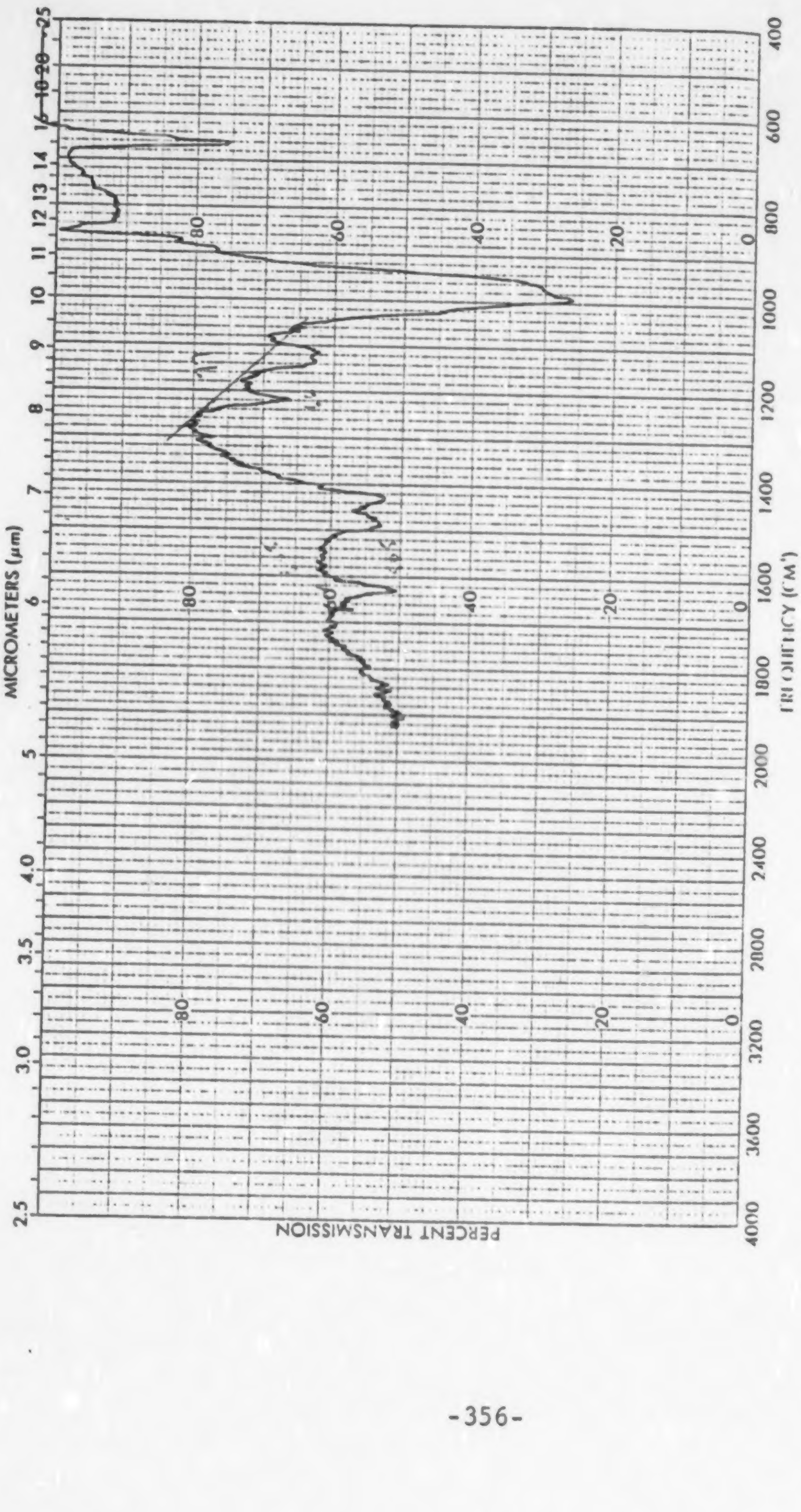


FIGURE F-72. INFRARED SPECTRA OF RTP HTS SOLIDS RUN MADE 30 JUNE - 3 JULY 1975

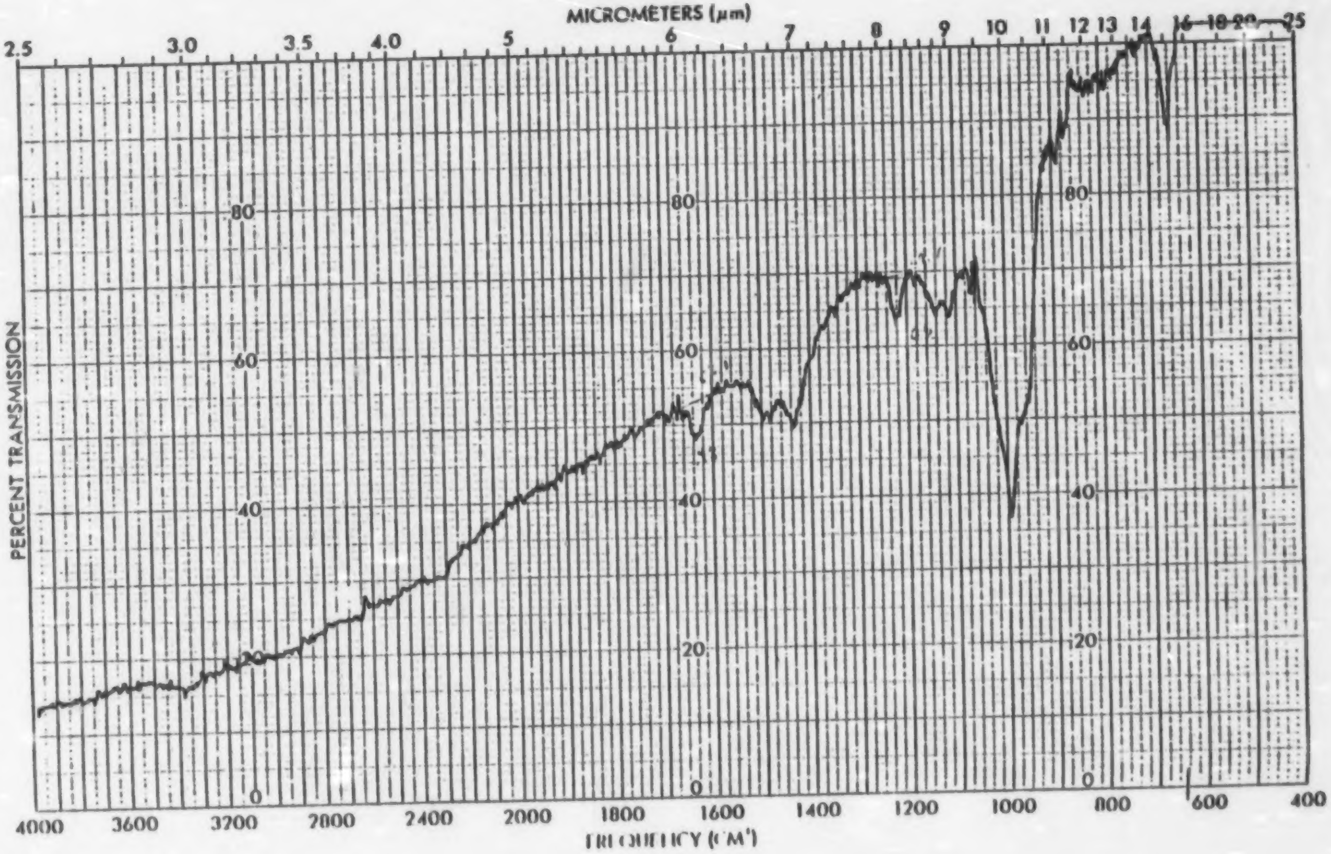


FIGURE F-73. INFRARED SPECTRA OF RTP HTS SOLIDS RUN MADE 30 JUNE - 3 JULY 1975

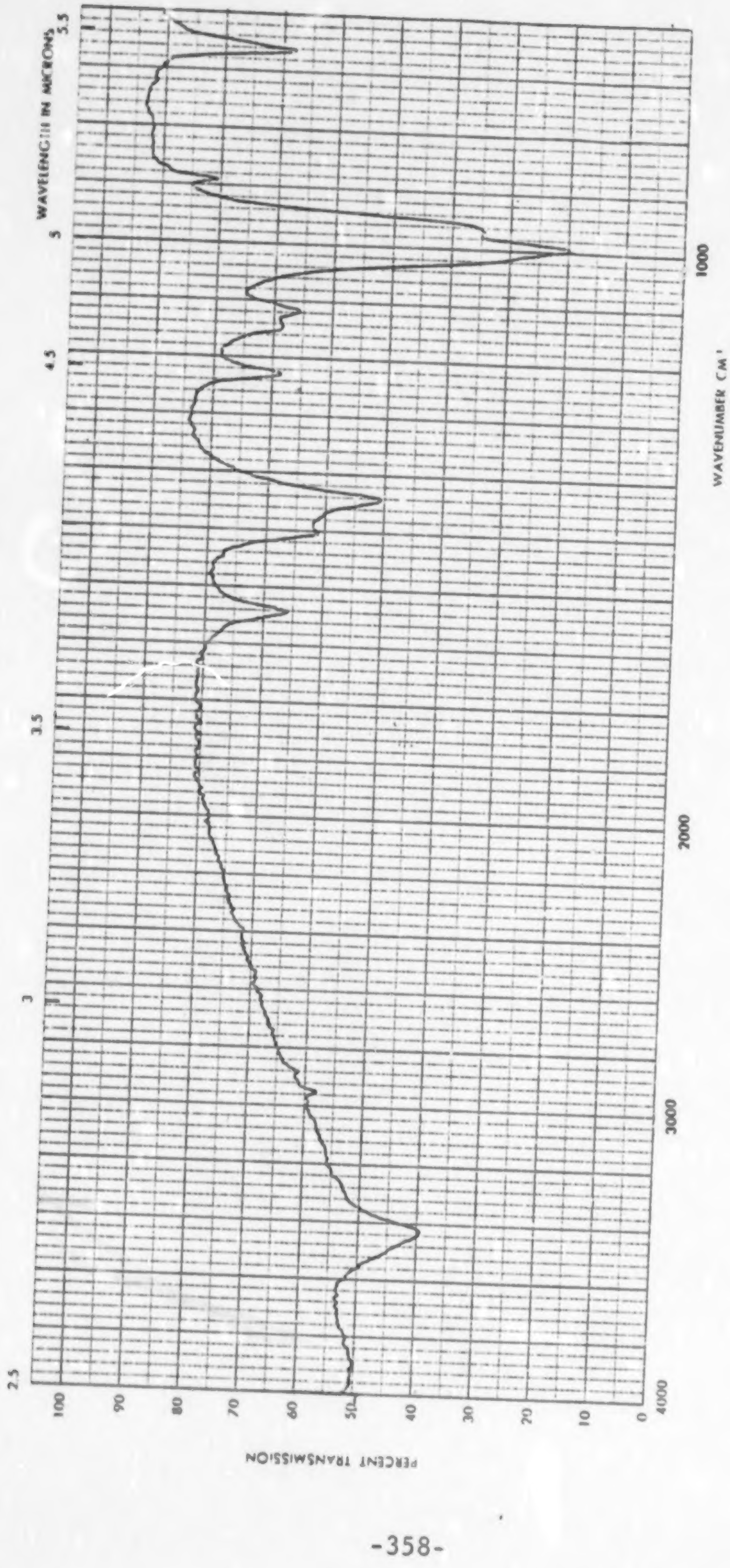


FIGURE F-74. INFRARED SPECTRA OF RTP CBS SOLIDS RUN
MADE 30 JUNE - 3 JULY 1975

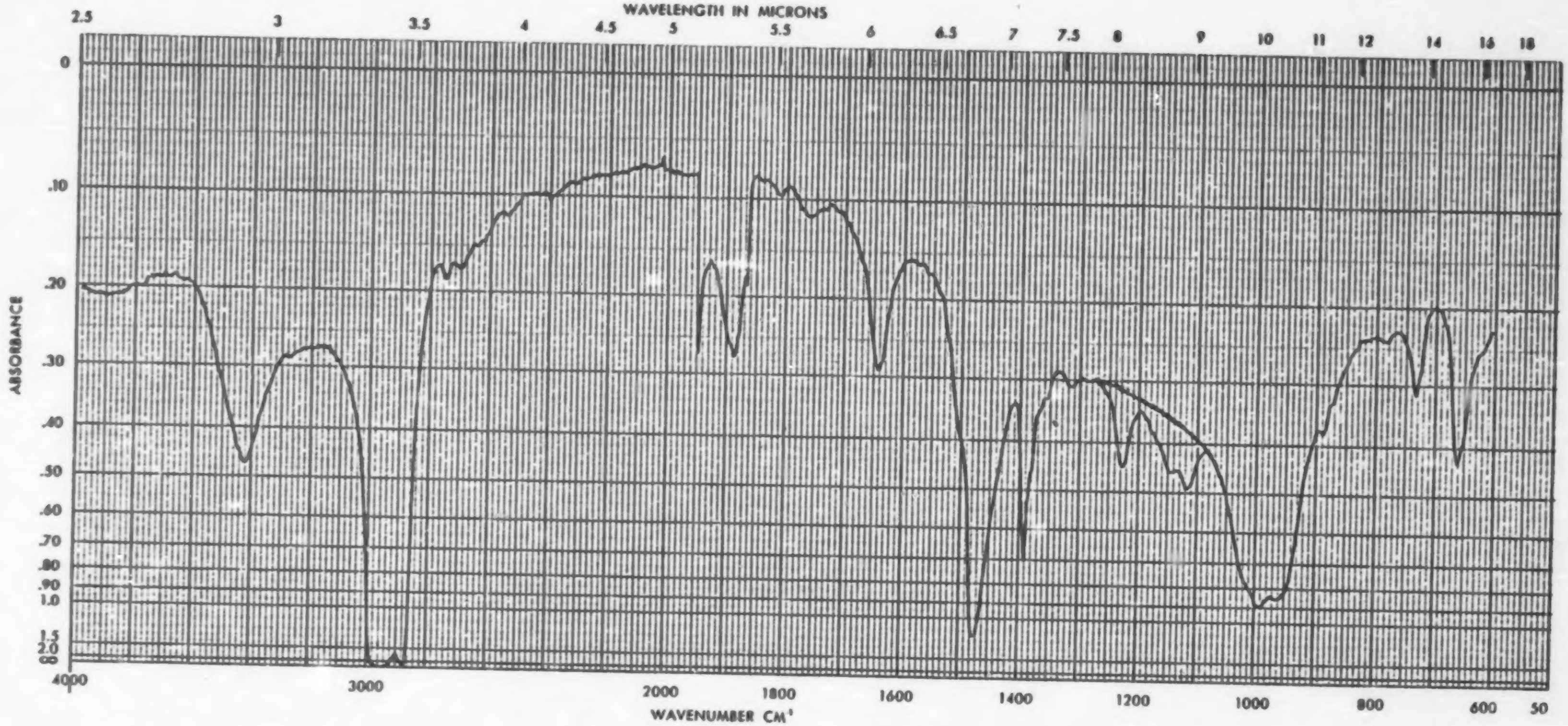


FIGURE F-75 INFRARED SPECTRA OF RTP CBS SOLIDS RUN
MADE 30 JUNE - 3 JULY 1975

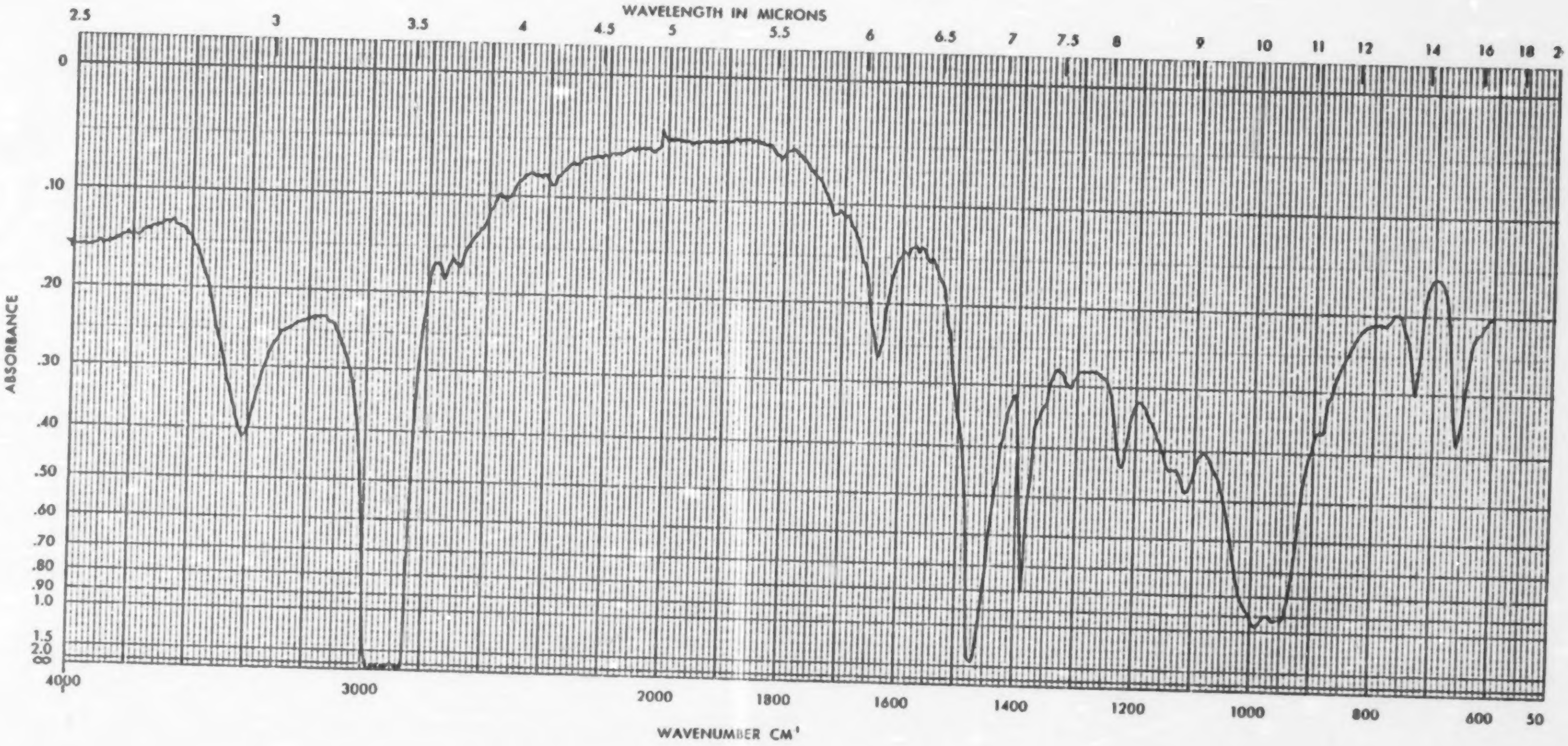


FIGURE F-76. INFRARED SPECTRA OF RTP CBS SOLIDS RUN
MADE 30 JUNE - 3 JULY 1975

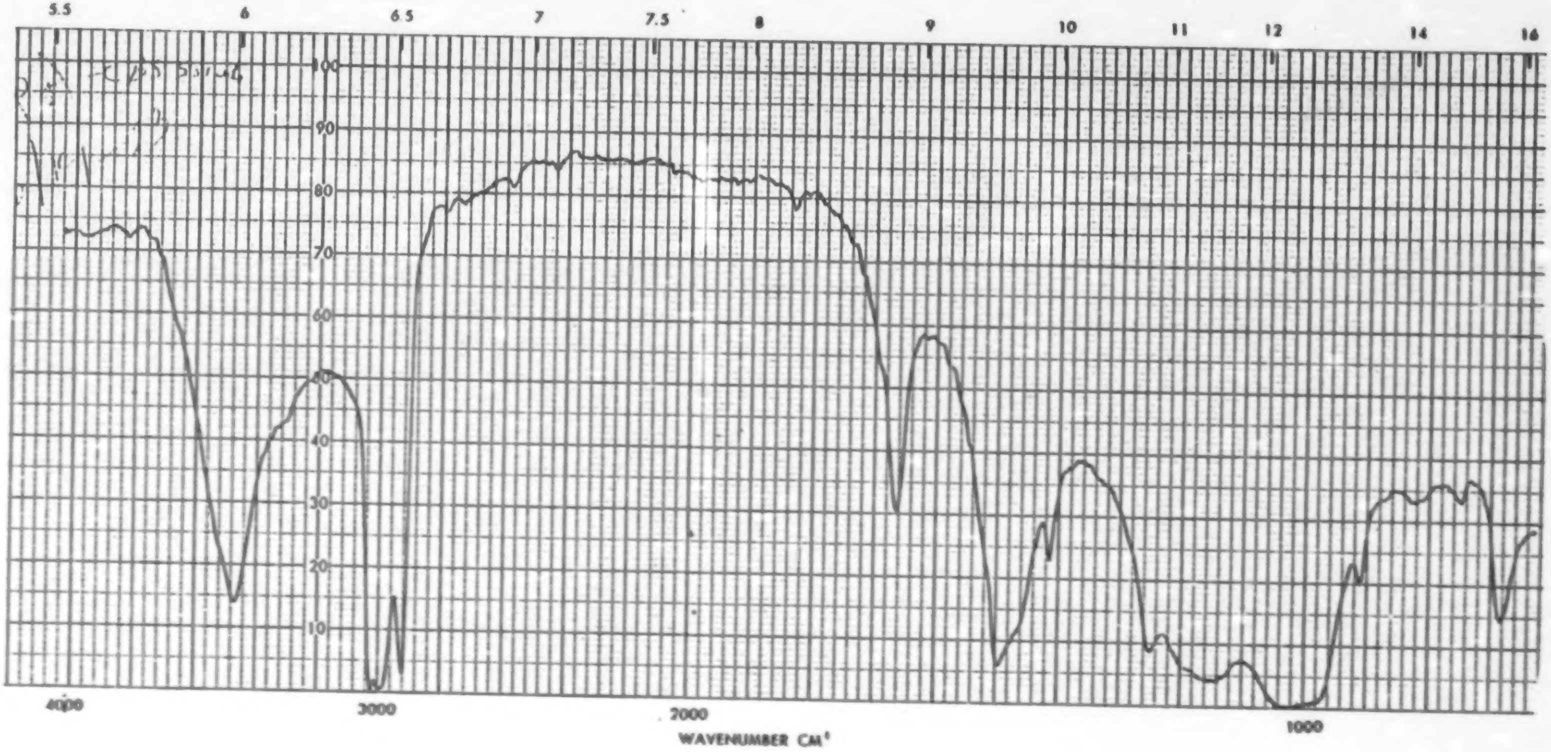


FIGURE F-77. INFRARED SPECTRA OF RTP CBS SOLIDS RUN
MADE 19-23 JUNE 1975

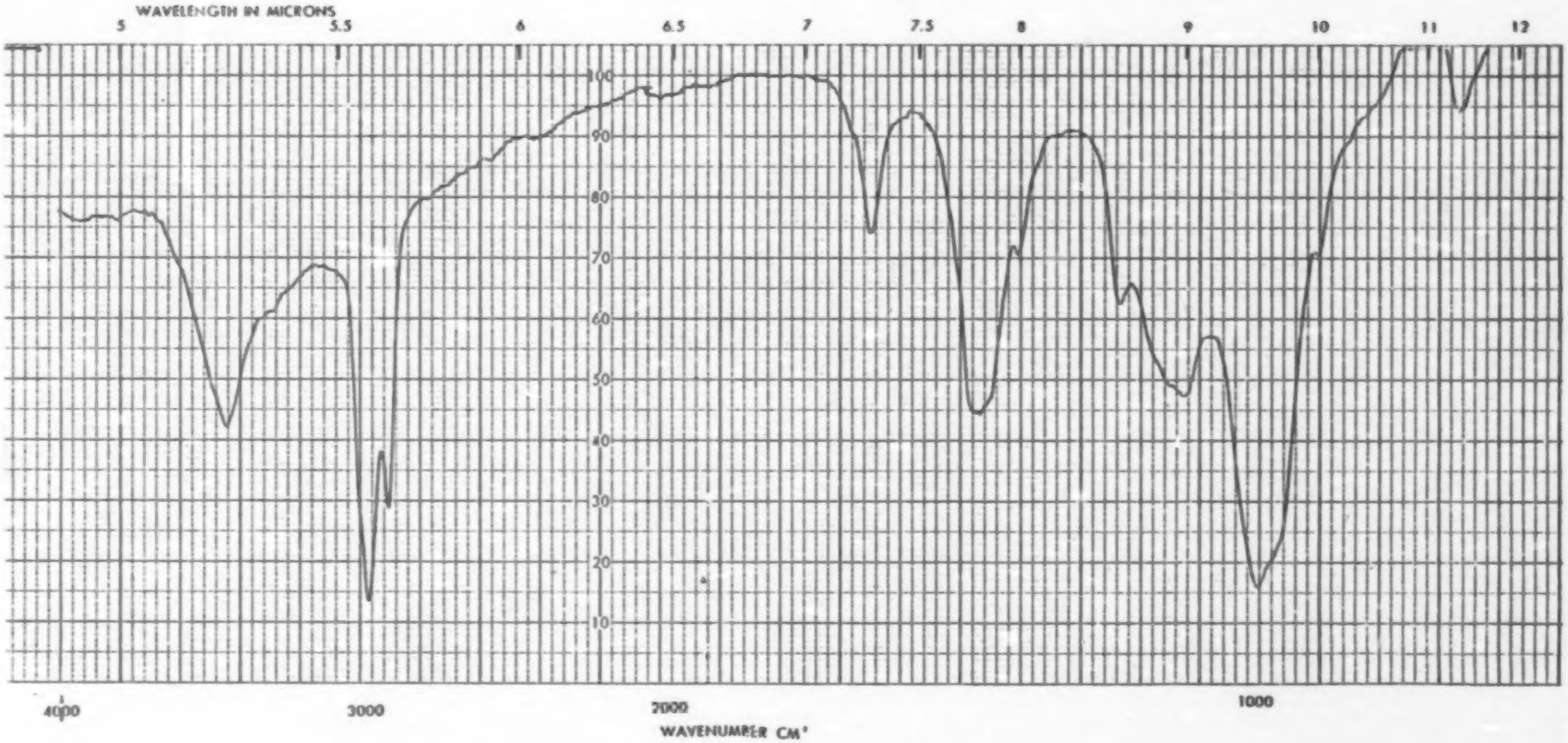


FIGURE F-78. INFRARED SPECTRA OF RTP HTS SOLIDS
RUN MADE 19-23 JUNE 1975

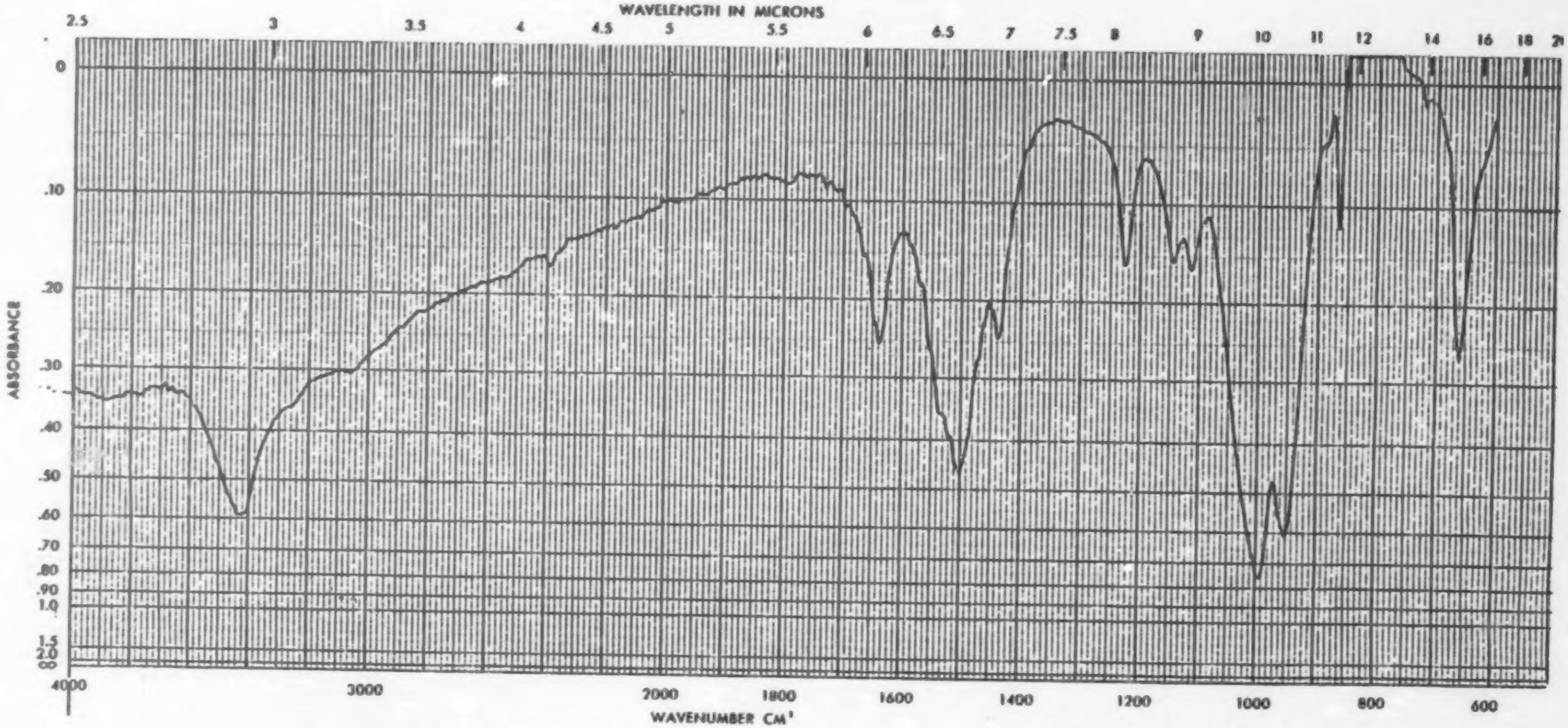


FIGURE F-79. INFRARED SPECTRA OF RTP HTL SOLIDS RUN
MADE 15-19 DECEMBER 1975

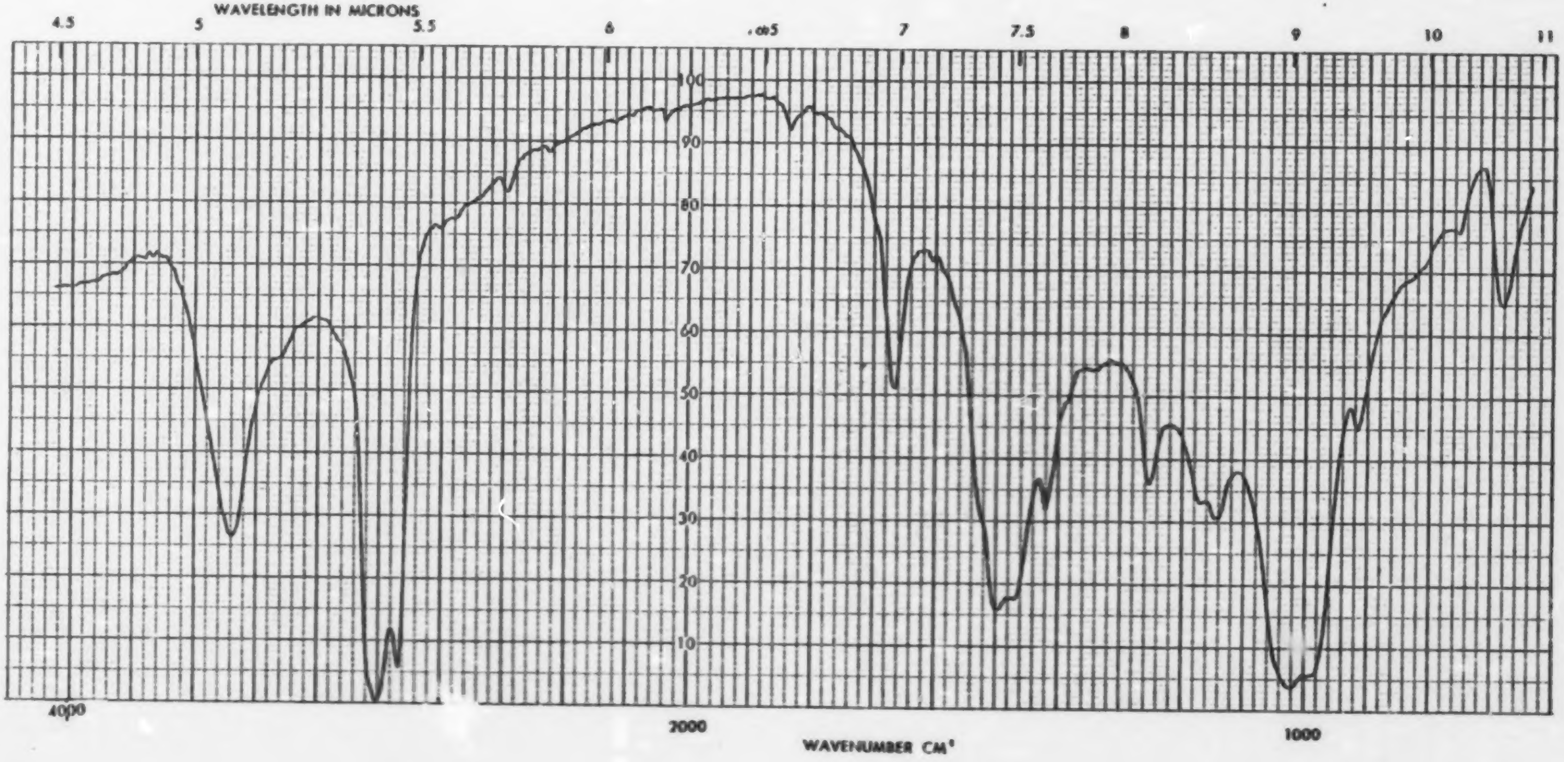


FIGURE F-80. INFRARED SPECTRA OF RTP CBS SOLIDS RUN
MADE 12-16 JANUARY 1976

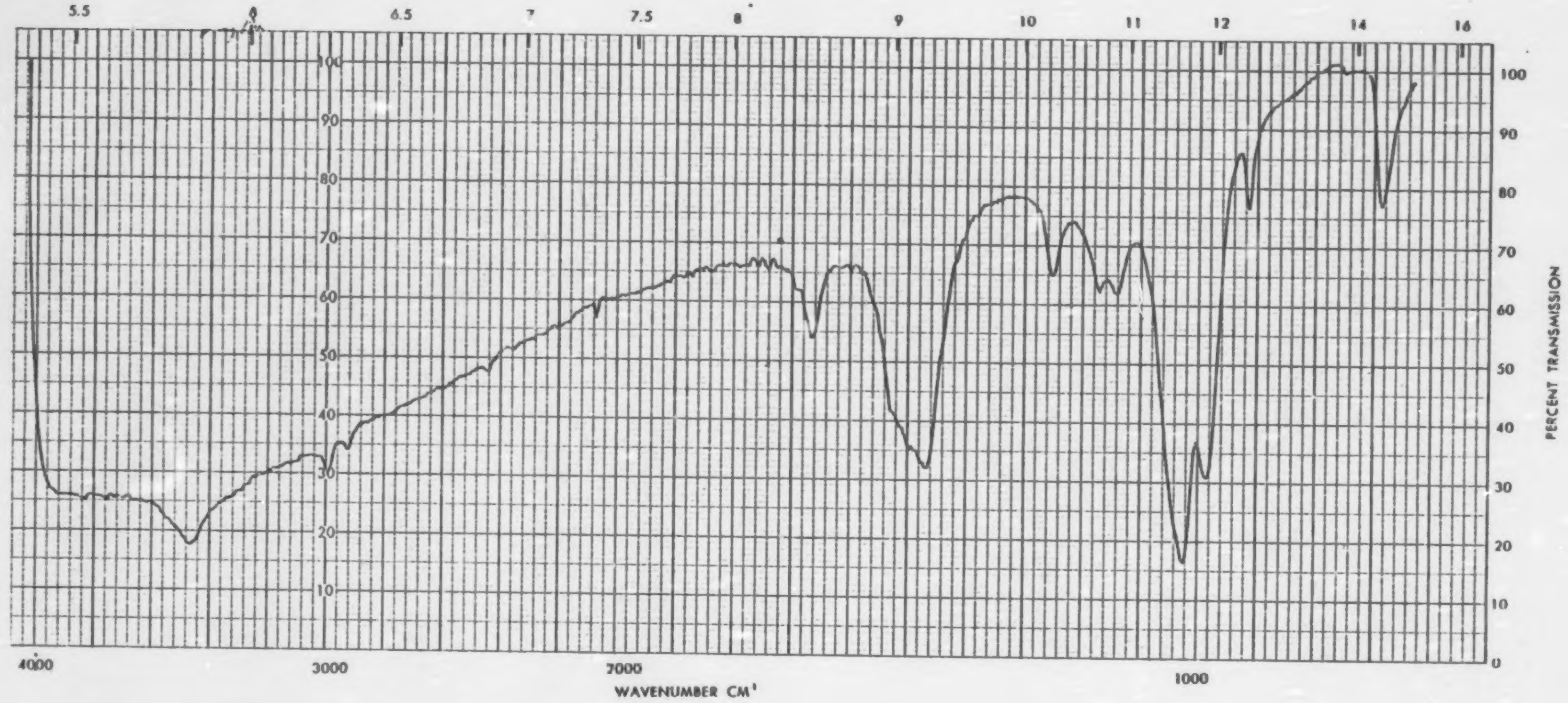


FIGURE F-81. INFRARED SPECTRA OF RTP CBS SOLIDS RUN
MADE 12-16 JANUARY 1976

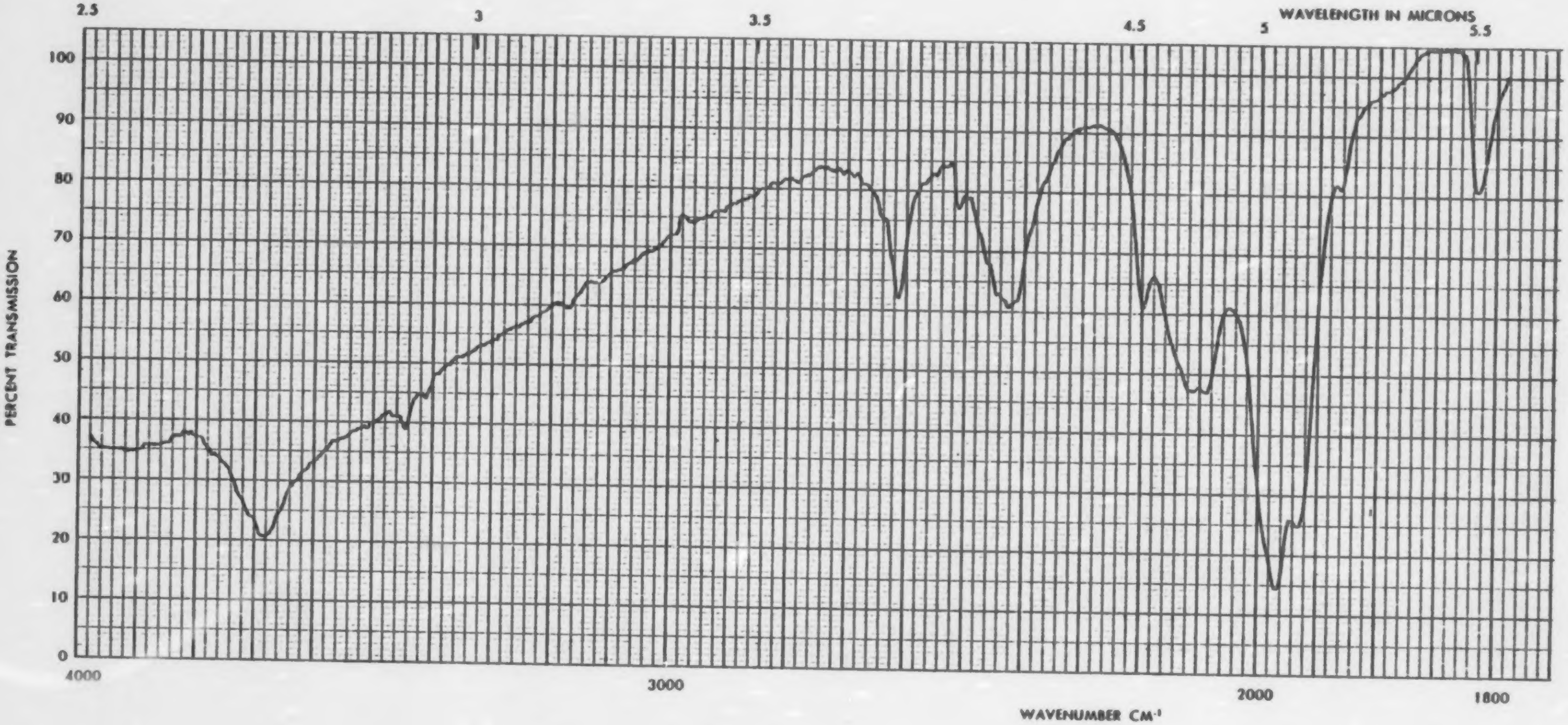


FIGURE F-82. INFRARED SPECTRA OF RTP CBS SOLIDS RUN MADE 19-23 JANUARY 1976

APPENDIX G

DIFFERENTIAL SCANNING CALORIMETRY PATTERNS OF PRECIPITATED SOLIDS

1.0 DESCRIPTION OF DIFFERENTIAL SCANNING CALORIMETRY PATTERNS

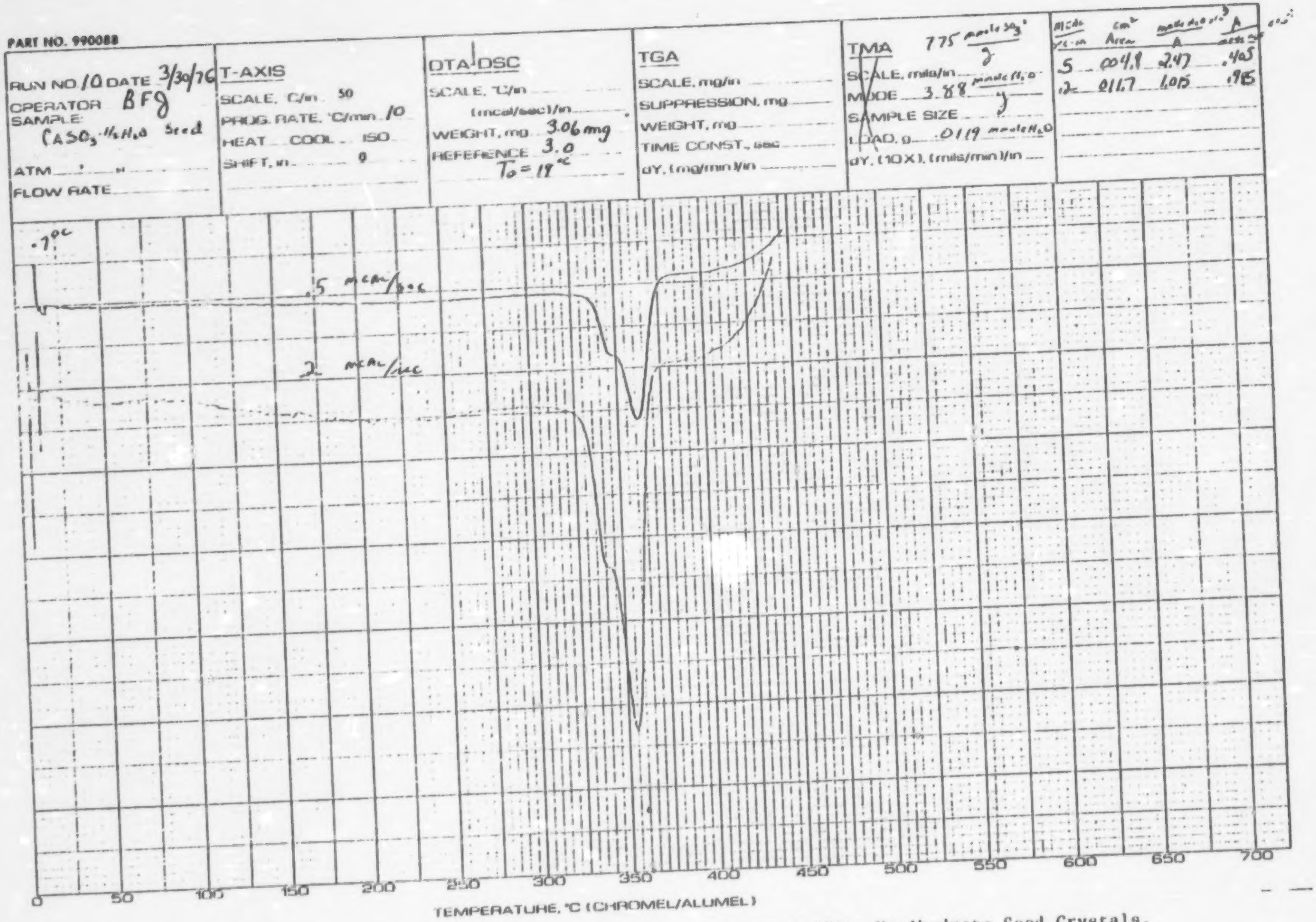
Two instrumental techniques based on the thermal properties of solids were utilized in characterizing the calcium sulfite-sulfate solid solution. Thermogravimetric analysis (TGA) was utilized to determine the weight change upon loss of water as the temperature is raised past the dehydration temperature. Both the weight loss and the temperature of dehydration are useful to characterize the solids.

Differential scanning calorimetry was also used to characterize the precipitated solids by monitoring the enthalpy change as a function of temperature. Phase changes, marked by rapid changes in the heat capacity, were observed in the temperature ranges of 120-140°C for gypsum and 350-430°C for calcium sulfite hemihydrate and the solid solutions. These changes represented by dips in the scans are associated with the loss of waters of hydration. If gypsum is not present in the solids, no enthalpy change will be observed at 120-140°C.

Three distinct patterns have been observed in the 350-430°C range which result from the dehydration of $CaSO_3 \cdot \frac{1}{2}H_2O$ and solid solution. These include an endothermic reaction at 410°C, and a complex endothermic reaction in the range of 350-400°C. Possible explanations for the three different patterns include a different crystal structure of the calcium sulfite hemihydrate resulting from impurities, such as sulfate, in the crystal and/or particle size. X-ray powder diffraction patterns have identified only one crystalline structure of calcium sulfite hemihydrate. This pattern is consistent with literature values (TE-055) and standards prepared in the laboratory. The complex endothermic reactions between 350-400°C were observed only in runs utilizing the grinder in line. This is a strong indication that particle size may have an effect on the temperature of dehydration of the calcium sulfite hemihydrate during analysis of DSC.

Actual scans of precipitated solids and standards by differential scanning calorimetry are presented in the remainder of this appendix. Two levels of sensitivity have been employed. Unless stated otherwise, the less sensitive scanning level is at 0.5 mcal/second, and the more sensitive scanning level is at 0.2 mcal/sec. In each run the less sensitive scan is the upper and the more sensitive scan is the lower one.

DIFFERENTIAL SCANNING CALORIMETRY PATTERNS OF PRECIPITATED SOLIDS



PART NO. 990088

RUN NO. 10 DATE 3/30/76
OPERATOR BFJ
SAMPLE: $CaSO_3 \cdot 1/2H_2O$ Seed
ATM
FLOW RATE

T-AXIS
SCALE, C/in 50
PROG. RATE, °C/min 10
HEAT COOL ISO
SHIFT, in 0

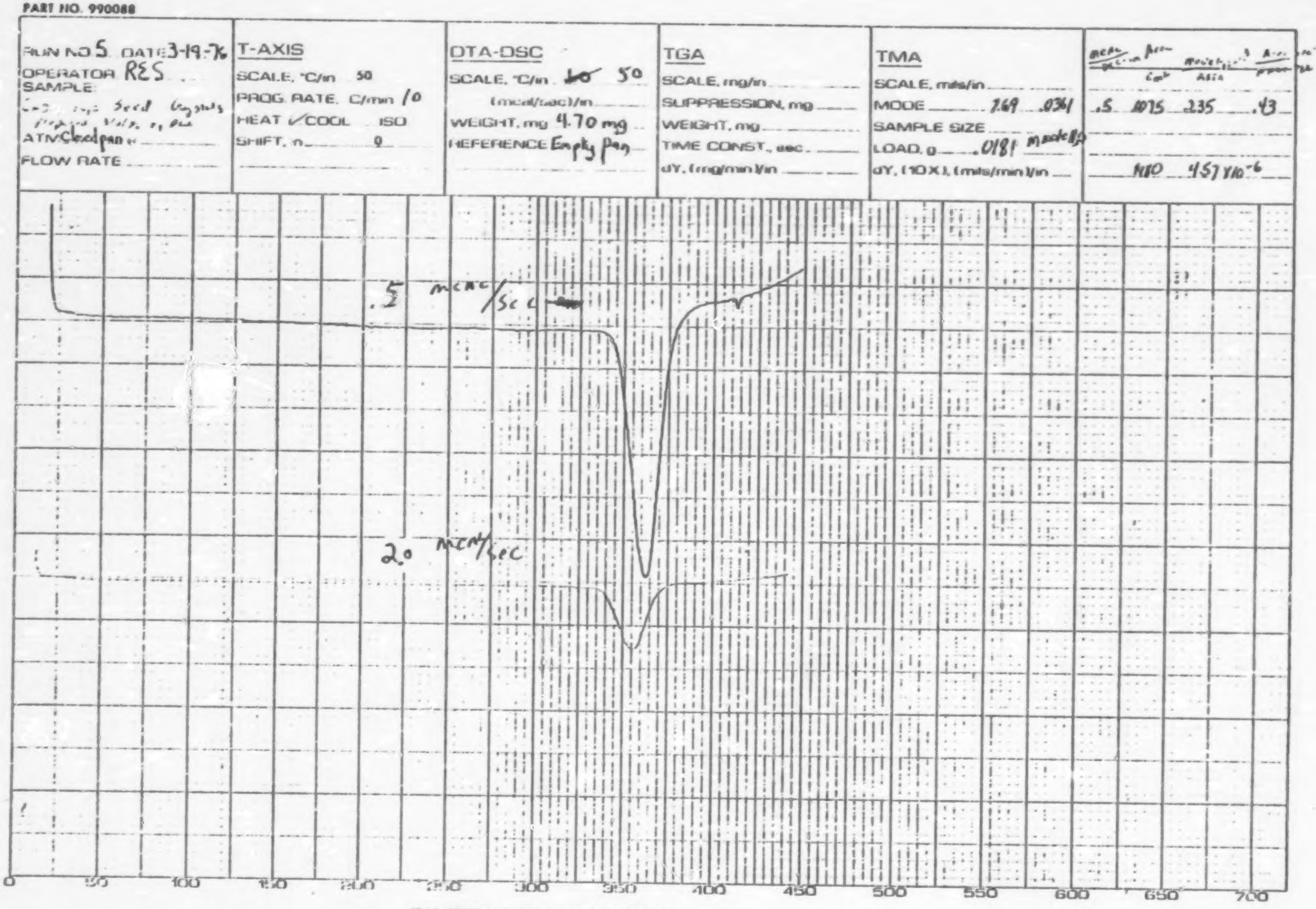
DTA DSC
SCALE, °C/in
(mcal/sec)/in
WEIGHT, mg 3.06 mg
REFERENCE 3.0
$T_0 = 19°C$

TGA
SCALE, mg/in
SUPPRESSION, mg
WEIGHT, mg
TIME CONST., sec
dY, (mg/min)/in

TMA 775 mole $SO_3^=$ / g
~~SCALE, mils/in~~
~~MODE~~ 3.88 mole H_2O / g
~~SAMPLE SIZE~~
~~LOAD, g~~ .0119 mole H_2O
dY, (10X), (mils/min)/in

Mcal/sec-in	cm² Area	mole H_2O/[illegible] A	A / mole [illegible]
5	004.8	2.47	.405
.2	011.7	1.015	.985

Figure G-1. Differential Calorimetry Scan of Calcium Sulfite Hemihydrate Seed Crystals.


PART NO. 990088

RUN NO 5 DATE 3-19-76
OPERATOR RES
SAMPLE: [illegible] Seed Crystals [illegible]
ATM Closed pan
FLOW RATE

T-AXIS
SCALE, °C/in 50
PROG. RATE, C/min 10
HEAT ✓ COOL ISO
SHIFT, in 0

DTA-DSC
SCALE, °C/in ~~10~~ 50
(mcal/sec)/in
WEIGHT, mg 4.70 mg
REFERENCE Empty Pan

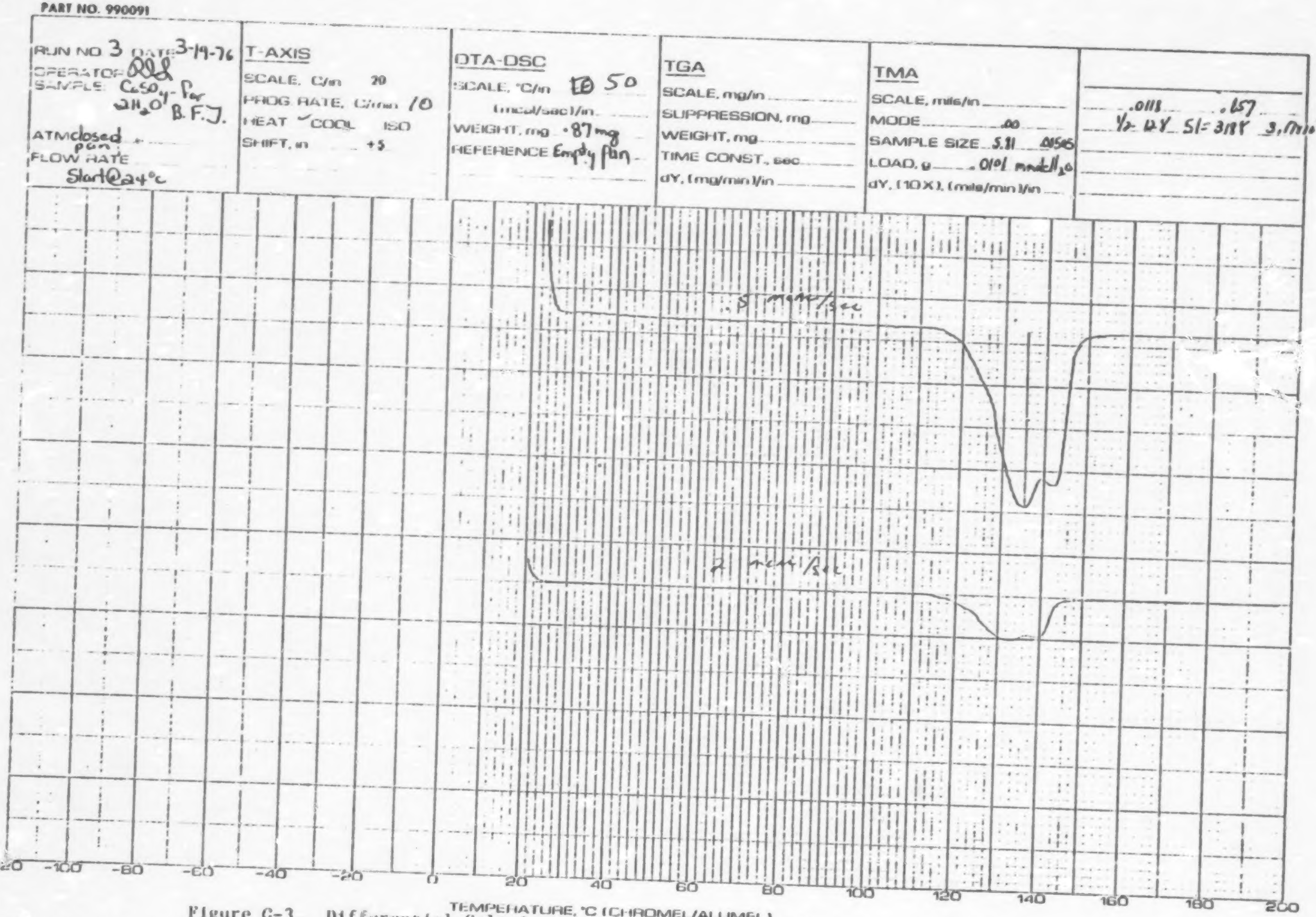
TGA
SCALE, mg/in
SUPPRESSION, mg
WEIGHT, mg
TIME CONST., sec
dY, (mg/min)/in

TMA
SCALE, mils/in
MODE 7.69 .0361
SAMPLE SIZE
LOAD, g .0181 [illegible]
dY, (10X), (mils/min)/in

[illegible]
.5 1075 .235 .43
1180 457×10⁻⁶

.5 mcal/sec
2.0 mcal/sec
0
50
100
150
200
250
300
350
400
450
500
550
600
650
700
TEMPERATURE, °C (CHROMEL/ALUMEL)

Figure G-2. Differential Calorimetry Scan of Calcium Sulfite Hemihydrate Seed Crystals.



PART NO. 990091

RUN NO 3 DATE 3-19-76
OPERATOR RLL
SAMPLE: $CaSO_4 \cdot \frac{1}{2}H_2O$ Par B.F.J.
ATM closed pan
FLOW RATE
Start@24°c

T-AXIS
SCALE, C/in 20
PROG RATE, C/min 10
HEAT ✓ COOL ISO
SHIFT, in +5

DTA-DSC
SCALE, °C/in ~~10~~ 50
(mcal/sec)/in
WEIGHT, mg .87 mg
REFERENCE Empty Pan

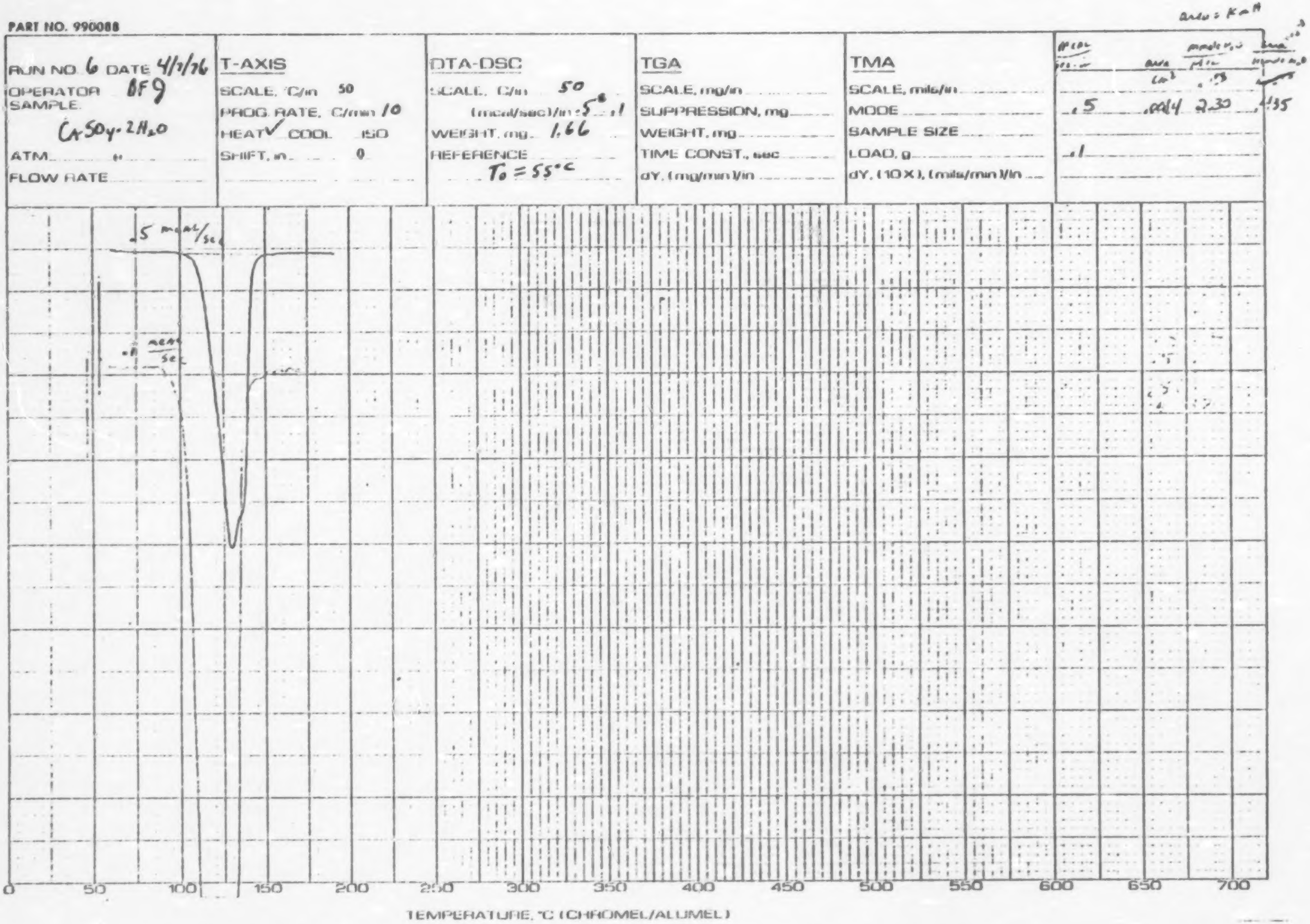
TGA
SCALE, mg/in
SUPPRESSION, mg
WEIGHT, mg
TIME CONST., sec
dY, (mg/min)/in

TMA
SCALE, mils/in
MODE .00
SAMPLE SIZE 5.11 .01505
LOAD, g .0101 mole H₂O
dY, (10X), (mils/min)/in

.0118 .157
½ H₂O 51 = 318 3,mole⁻⁶

.5 mcal/sec
2 mcal/sec
-120
-100
-80
-60
-40
-20
0
20
40
60
80
100
120
140
160
180
200
TEMPERATURE, °C (CHROMEL/ALUMEL)

Figure G-3. Differential Calorimetry Scan of Calcium Sulfite Hemihydrate Seed Crystals.



PART NO. 990088

RUN NO. 6 DATE 4/7/76
OPERATOR BFG
SAMPLE
$CaSO_4 \cdot 2H_2O$
ATM ''
FLOW RATE

T-AXIS
SCALE, °C/in 50
PROG. RATE, °C/min 10
HEAT ✓ COOL 150
SHIFT, in. 0

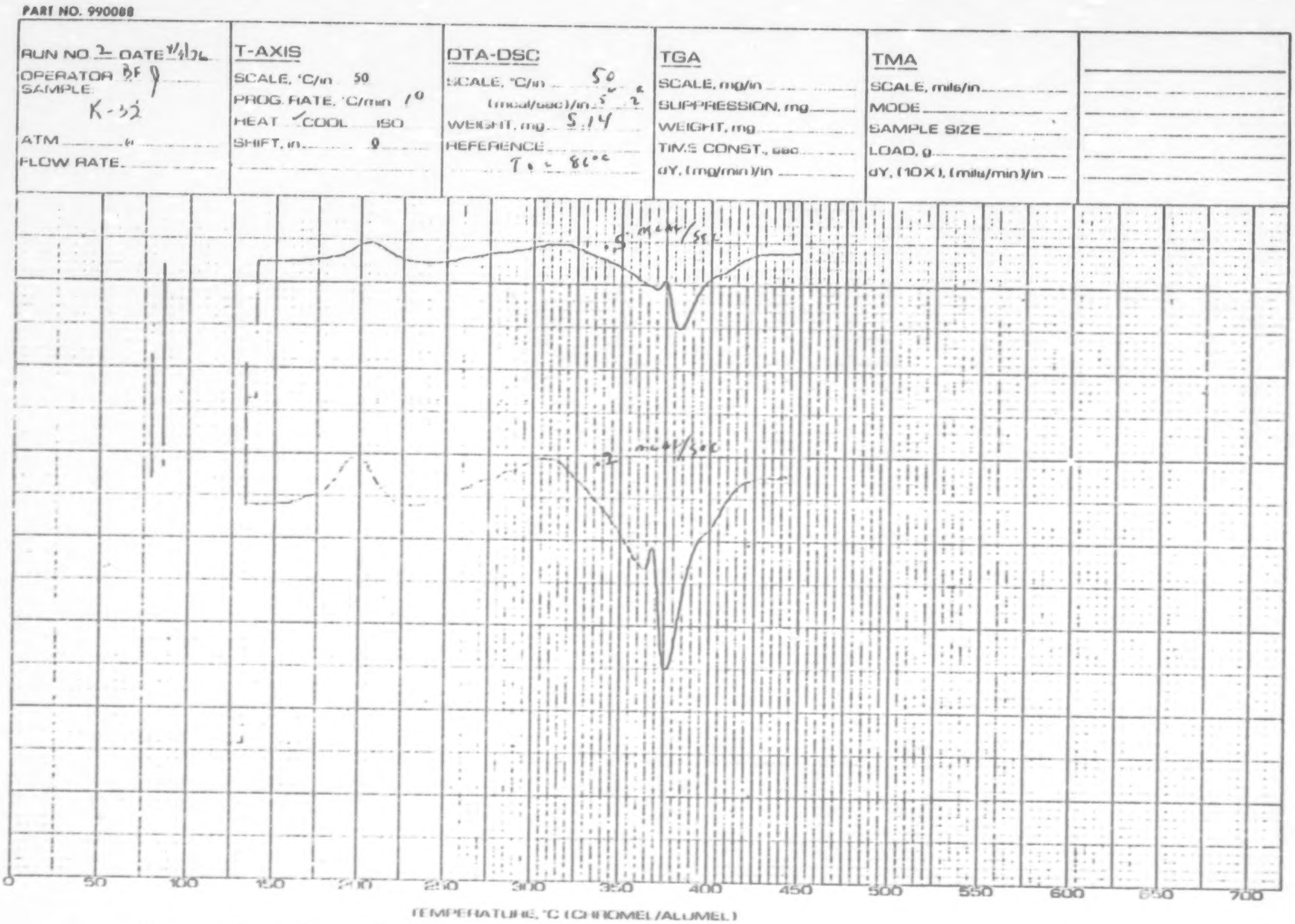
DTA-DSC
SCALE, °C/in 50
(mcal/sec)/in 5 .1
WEIGHT, mg 1.66
REFERENCE
$T_0 = 55°C$

TGA
SCALE, mg/in
SUPPRESSION, mg
WEIGHT, mg
TIME CONST., sec
dY, (mg/min)/in

TMA
SCALE, mils/in
MODE
SAMPLE SIZE
LOAD, g
dY, (10X), (mils/min)/in

.5 .0014 2.30 .435
.1

Figure G-4. Differential Calorimetry Scan of Gypsum or Calcium Sulfate Dihydrate.



PART NO. 990088

RUN NO 2 DATE 4/1/76
OPERATOR BF J
SAMPLE K-32
ATM
FLOW RATE

T-AXIS
SCALE, °C/in 50
PROG. RATE, °C/min 10
HEAT ✓ COOL ISO
SHIFT, in. 0

DTA-DSC
SCALE, °C/in 50
(mcal/sec)/in .5 .2
WEIGHT, mg 5.14
REFERENCE
T₀ = 86°C

TGA
SCALE, mg/in
SUPPRESSION, mg
WEIGHT, mg
TIME CONST., sec
dY, (mg/min)/in

TMA
SCALE, mils/in
MODE
SAMPLE SIZE
LOAD, g
dY, (10X), (mils/min)/in

Figure G-5. Differential Calorimetry Scan of Solids Precipitated from Kinetic Run No. 32

PART NO. 990088

RUN NO. ___ DATE 4/21/76	**T-AXIS**	**DTA-DSC**	**TGA**	**TMA**	
OPERATOR BFJ	SCALE, °C/in 50	SCALE, °C/in 50	SCALE, mg/in	SCALE, mils/in	
SAMPLE: K-32	PROG. RATE, °C/min 10	(mcal/sec)/in $6^{.5}$ $8^{.2}$	SUPPRESSION, mg	MODE	
ATM. AR 4	HEAT ✓ COOL ISO	WEIGHT, mg 8.00	WEIGHT, mg	SAMPLE SIZE	
FLOW RATE	SHIFT, in 0	REFERENCE	TIME CONST., sec	LOAD, g	
		T_0 = 23	dY, (mg/min)/in	dY, (10X), (mils/min)/in	

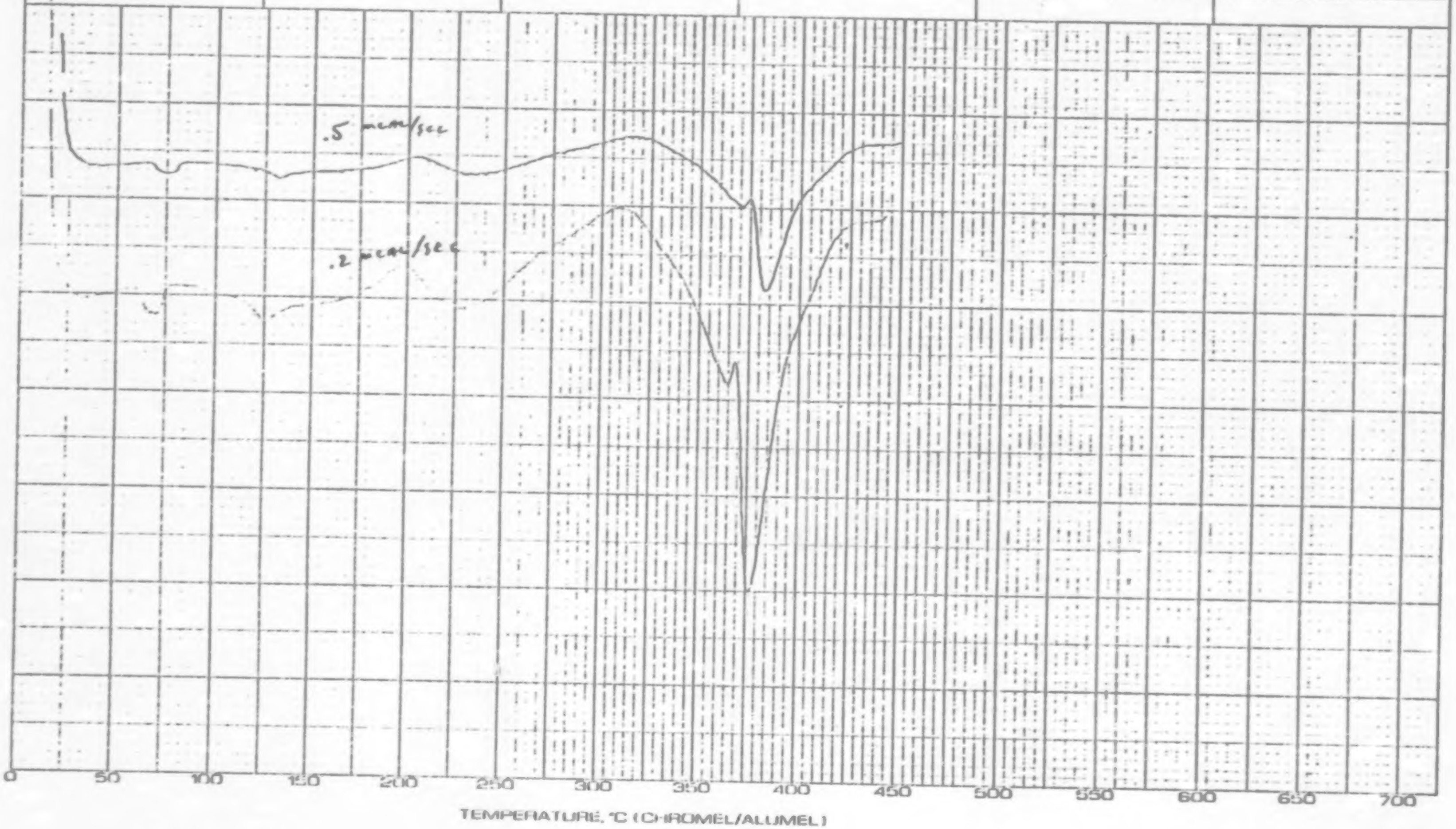
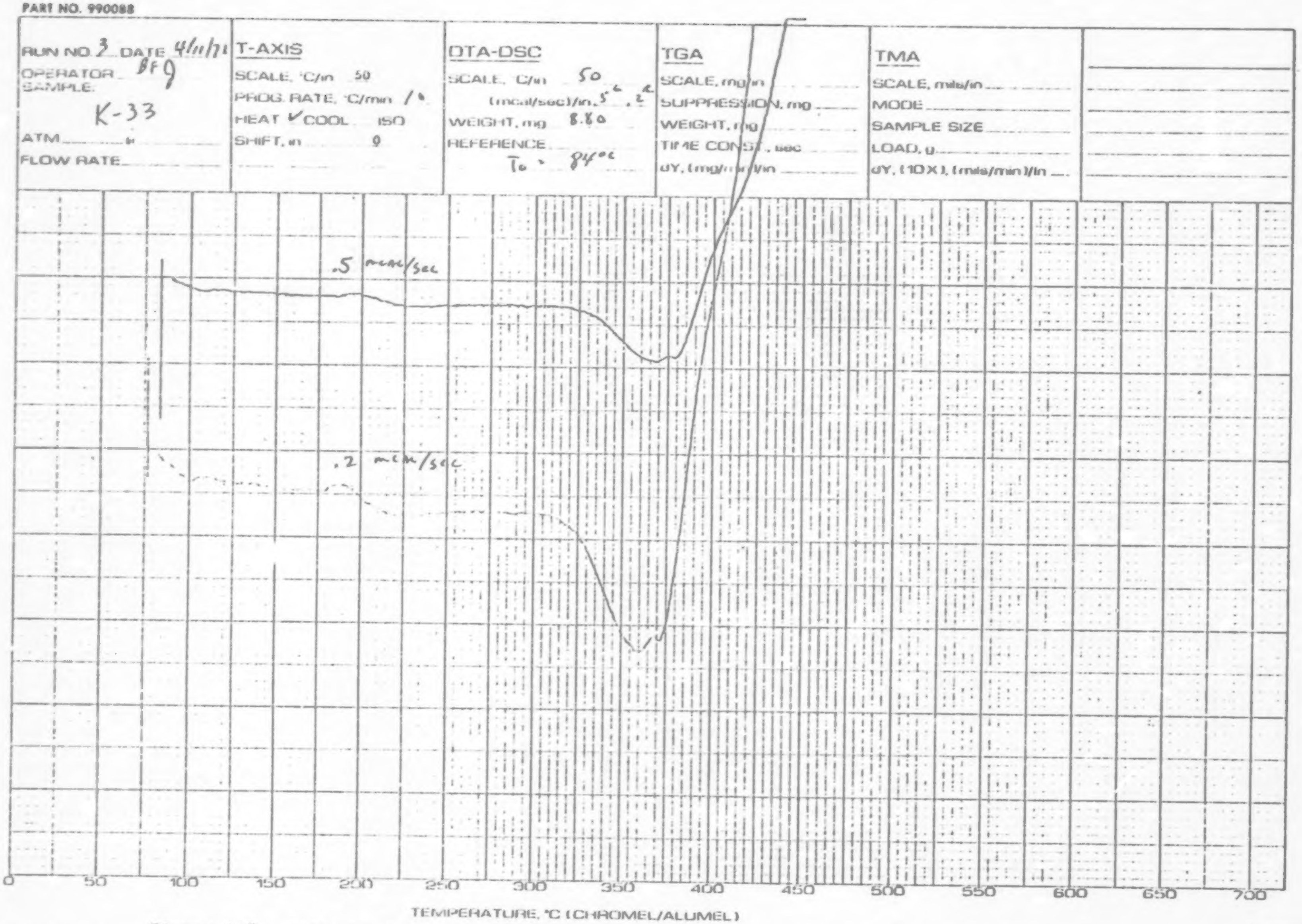


Figure G-6. Differential Calorimetry Scan of Solids Precipitated from Kinetic Run No. 32



PART NO. 990088

RUN NO. 3 DATE 4/11/71
OPERATOR BFG
SAMPLE:
K-33
ATM
FLOW RATE

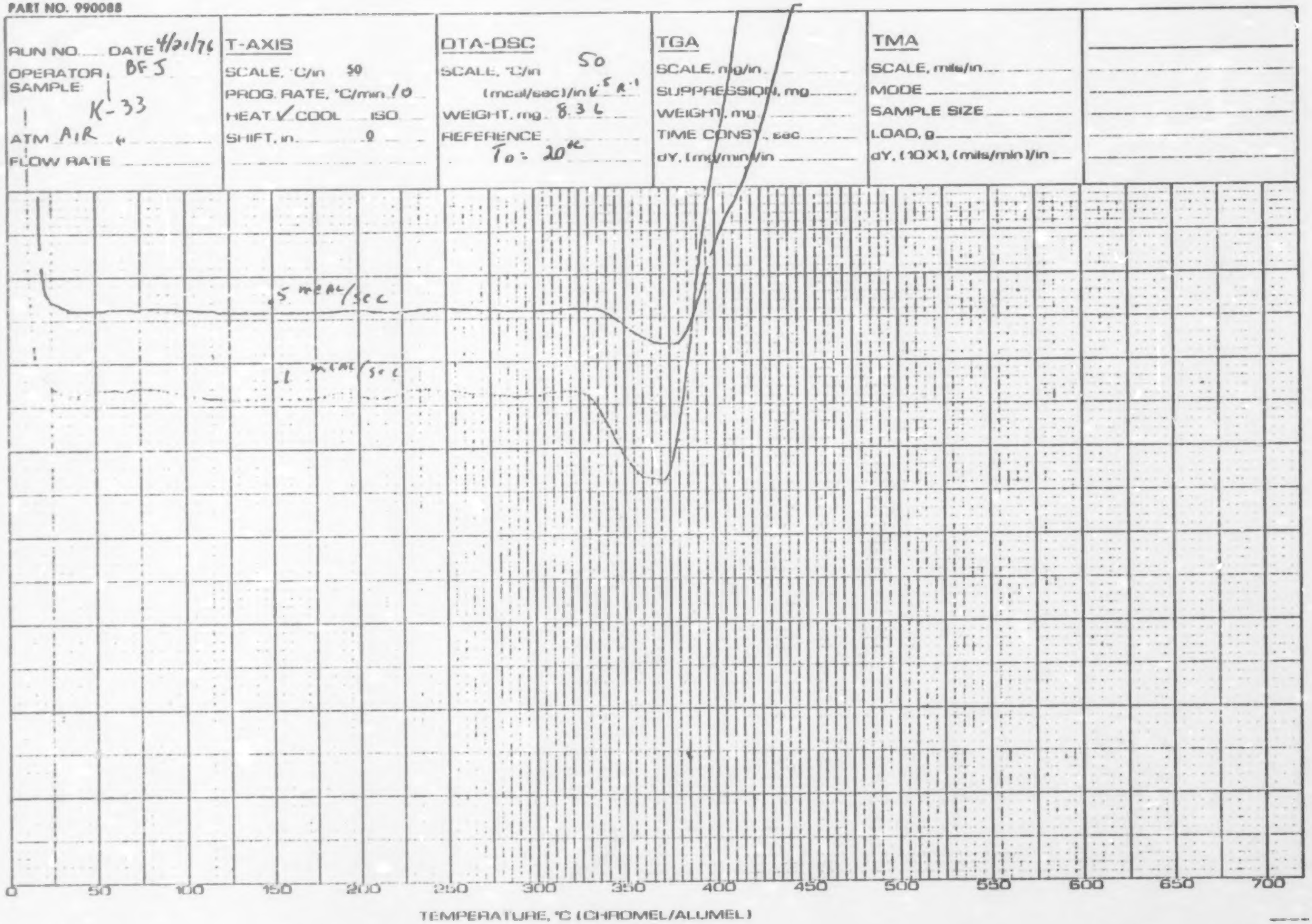
T-AXIS
SCALE, °C/in 50
PROG. RATE, °C/min 10
HEAT ✓ COOL ISO
SHIFT, in 0

DTA-DSC
SCALE, °C/in 50
(mcal/sec)/in. 5c .2c
WEIGHT, mg 8.80
REFERENCE
To = 84°C

TGA
SCALE, mg/in
SUPPRESSION, mg
WEIGHT, mg
TIME CONST., sec
dY, (mg/min)/in

TMA
SCALE, mils/in
MODE
SAMPLE SIZE
LOAD, g
dY, (10X), (mils/min)/in

Figure C-7. Differential Calorimetry Scan of Solids Precipitated from Kinetic Run No. 33



PART NO. 990088

RUN NO. ____ DATE 4/21/76
OPERATOR BFJ
SAMPLE K-33
ATM AIR
FLOW RATE ____

T-AXIS
SCALE, °C/in 50
PROG. RATE, °C/min 10
HEAT ✓ COOL ____ ISO ____
SHIFT, in. 0

DTA-DSC
SCALE, °C/in 50
(mcal/sec)/in & .5 & .1
WEIGHT, mg 8.36
REFERENCE T_0 = 20°C

TGA
SCALE, mg/in ____
SUPPRESSION, mg ____
WEIGHT, mg ____
TIME CONST., sec ____
dY, (mg/min)/in ____

TMA
SCALE, mils/in ____
MODE ____
SAMPLE SIZE ____
LOAD, g ____
dY, (10X), (mils/min)/in ____

Figure C-8. Differential Calorimetry Scan of Solids Precipitated from Kinetic Run No. 33

PART NO. 990088

RUN NO 3 DATE 3-24-76
OPERATOR [illegible]
SAMPLE: Run #34 Solids D.L.H.
ATM Covered pan
FLOW RATE

T-AXIS
SCALE, °C/in 50
PROG. RATE, C/min 10
HEAT COOL ISO
SHIFT, in 0

DTA-DSC
SCALE, °C/in ~~10~~ 50
(mcal/sec)/in
WEIGHT, mg 4.00 mg
REFERENCE Empty pan

TGA
SCALE, mg/in
SUPPRESSION, mg
WEIGHT, mg
TIME CONST., sec
dY, (mg/min)/in

TMA
SCALE, mils/in
MODE 2.70 .0108
SAMPLE SIZE .41 .0024
LOAD, g
dY, (10X), (mils/min)/in

mcal/sec·in cm² mcal/sec [illegible]
.5 3.0 22 .45
551 24×10⁻⁶

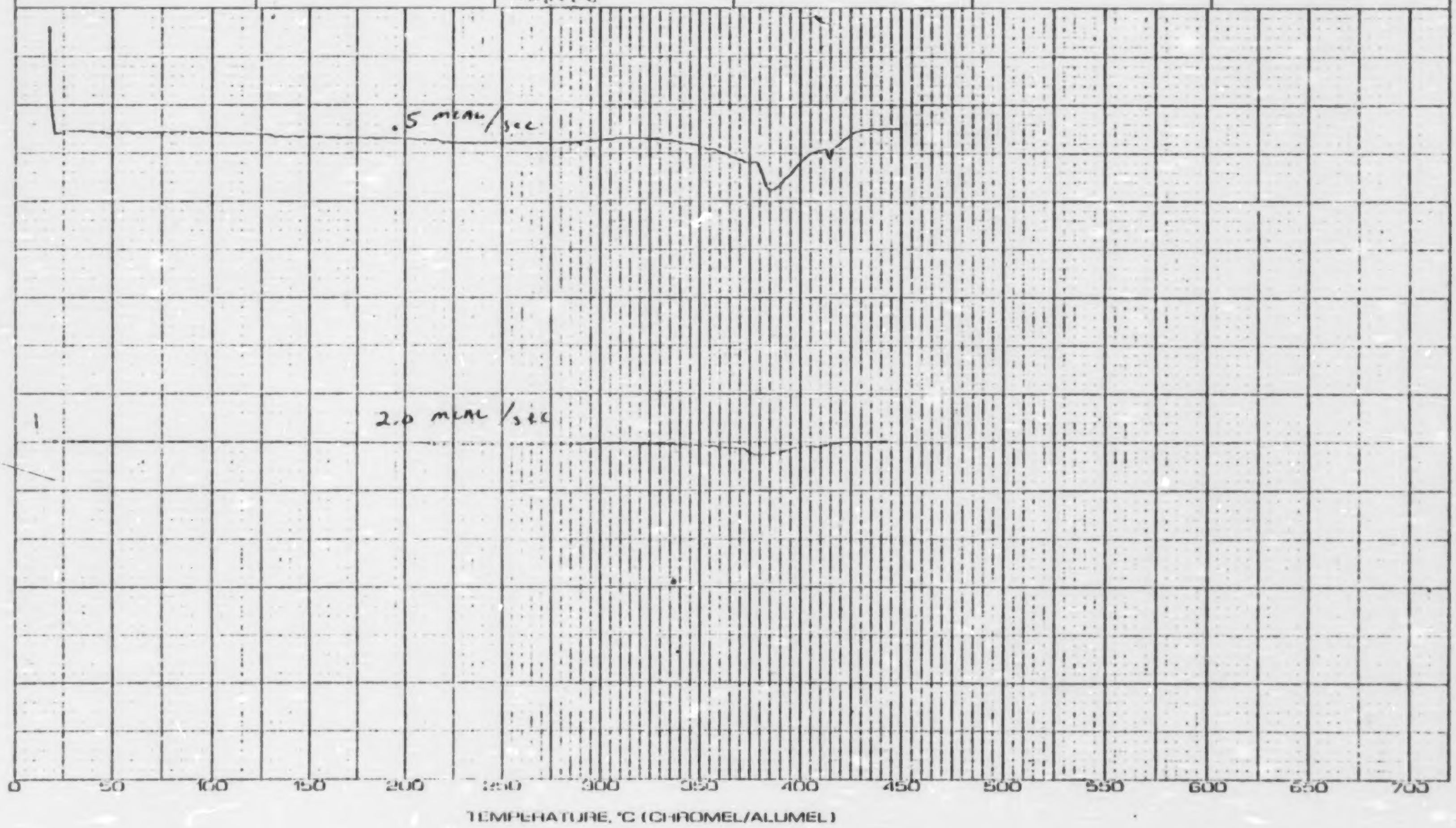


Figure C-9. Differential Calorimetry Scan of Solids Precipitated from Kinetic Run No. 34

PART NO. 990088

RUN NO. ___ DATE 4/21/76
OPERATOR BFQ
SAMPLE: K-35
ATM AIR
FLOW RATE

T-AXIS
SCALE, °C/in 50
PROG. RATE, °C/min 10
HEAT ✓ COOL ISO
SHIFT, in 0

DTA-DSC
SCALE, °C/in 50
(mcal/sec)/in 6.5 R^{-2}
WEIGHT, mg 9.81
REFERENCE
T₀ = 20 °C
CORRECTION = +5 °C

TGA
SCALE, mg/in
SUPPRESSION, mg
WEIGHT, mg
TIME CONST., sec
dY, (mg/min)/in

TMA
SCALE, mils/in
MODE
SAMPLE SIZE
LOAD, g
dY, (10X), (mils/min)/in

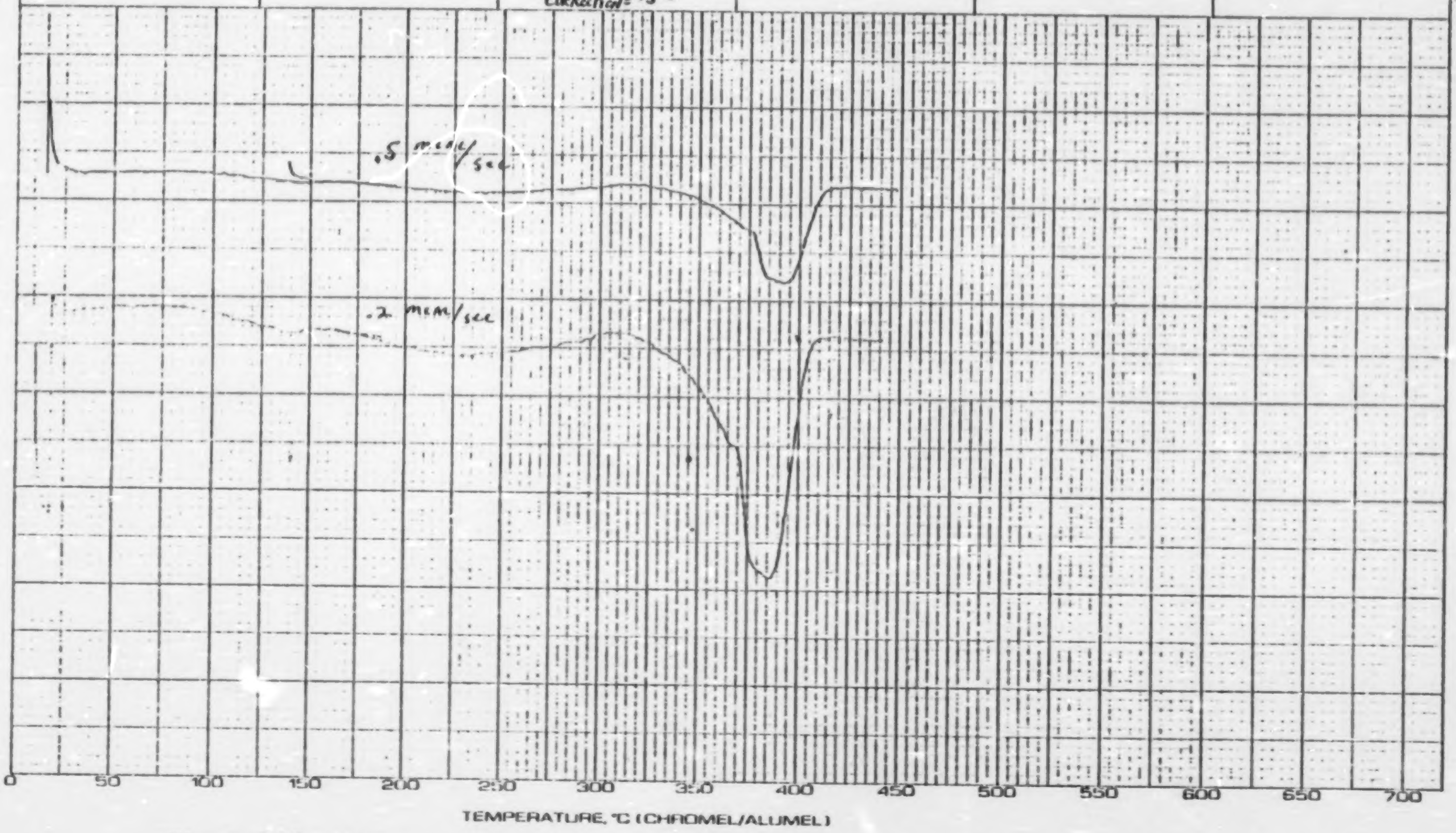
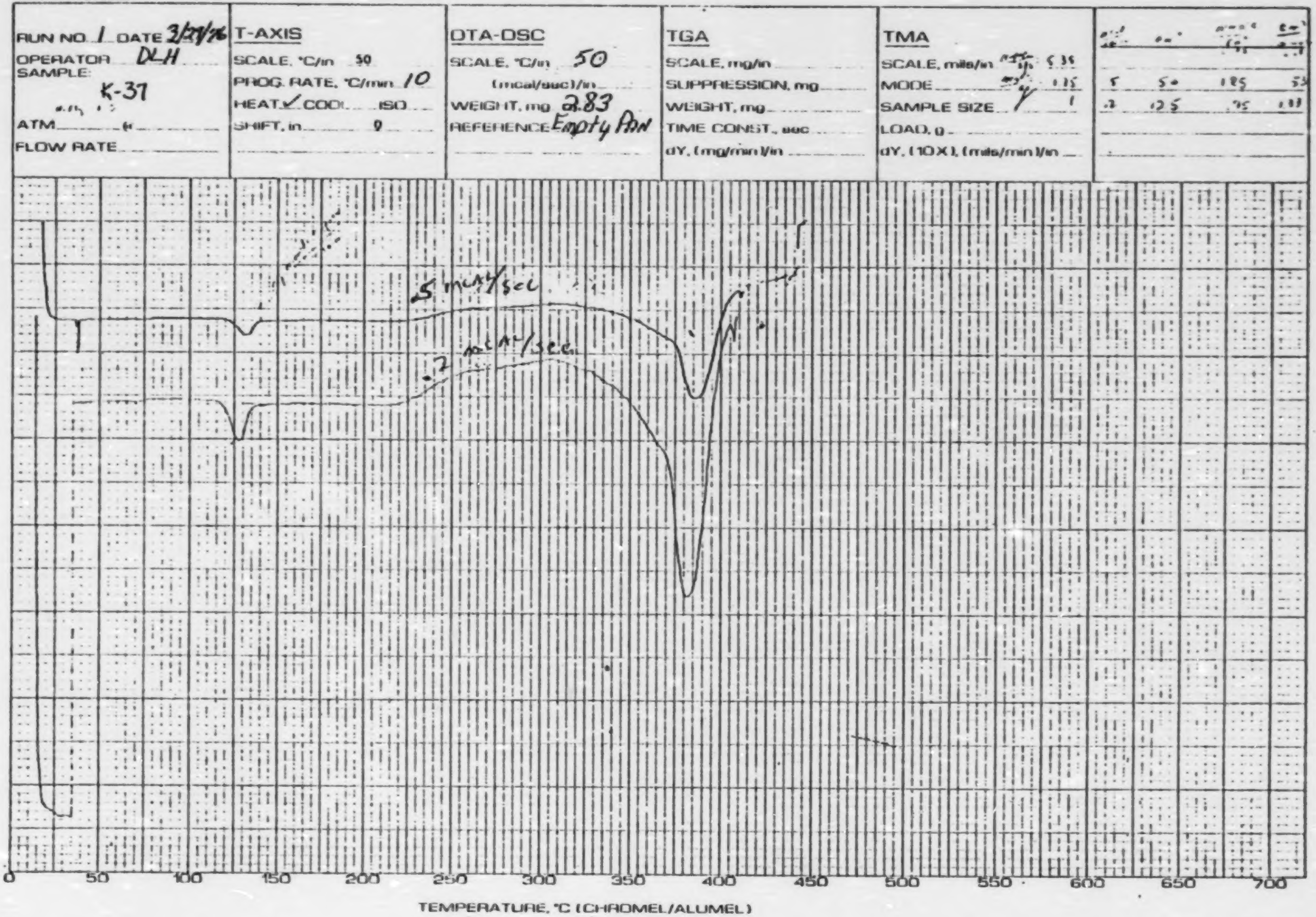


Figure C-10. Differential Calorimetry Scan of Solids Precipitated from Kinetic Run No. 35

PART NO. 990088



RUN NO. 1 DATE 3/29/76
OPERATOR DLH
SAMPLE: K-37
ATM
FLOW RATE

T-AXIS
SCALE, °C/in 50
PROG. RATE, °C/min 10
HEAT ✓ COOL ISO
SHIFT, in 0

DTA-DSC
SCALE, °C/in 50
(mcal/sec)/in
WEIGHT, mg 2.83
REFERENCE Empty Pan

TGA
SCALE, mg/in
SUPPRESSION, mg
WEIGHT, mg
TIME CONST., sec
dY, (mg/min)/in

TMA
SCALE, mils/in 5.35
MODE 1.15
SAMPLE SIZE 1
LOAD, g
dY, (10X), (mils/min)/in

5 50 185 53
.3 12.5 .75 1.1

Figure G-11. Differential Calorimetry Scan of Solids Precipitated from Kinetic Run No. 37

PART NO. 990088

RUN NO. 3 DATE 3-22-76
OPERATOR jhcw
SAMPLE Rm #40 solids
K-40 DL.H.
ATM Covered pan
FLOW RATE

T-AXIS
SCALE, °C/in 50
PROG RATE, C/min 10
HEAT COOL ISO
SHIFT, in 0

DTA-DSC
SCALE, °C/in ~~10~~ 50
(mcal/sec)/in
WEIGHT, mg 3.63
REFERENCE Empty pan

TGA
SCALE, mg/in
SUPPRESSION, mg
WEIGHT, mg
TIME CONST, sec
dY, (mg/min)/in

TMA
SCALE, mils/in
MODE .261=X50
SAMPLE SIZE .286=X60
LOAD, g
dY, (10X), (mils/min)/in

.5	.0025	.261	.373
.6	.0075	2.77	.361

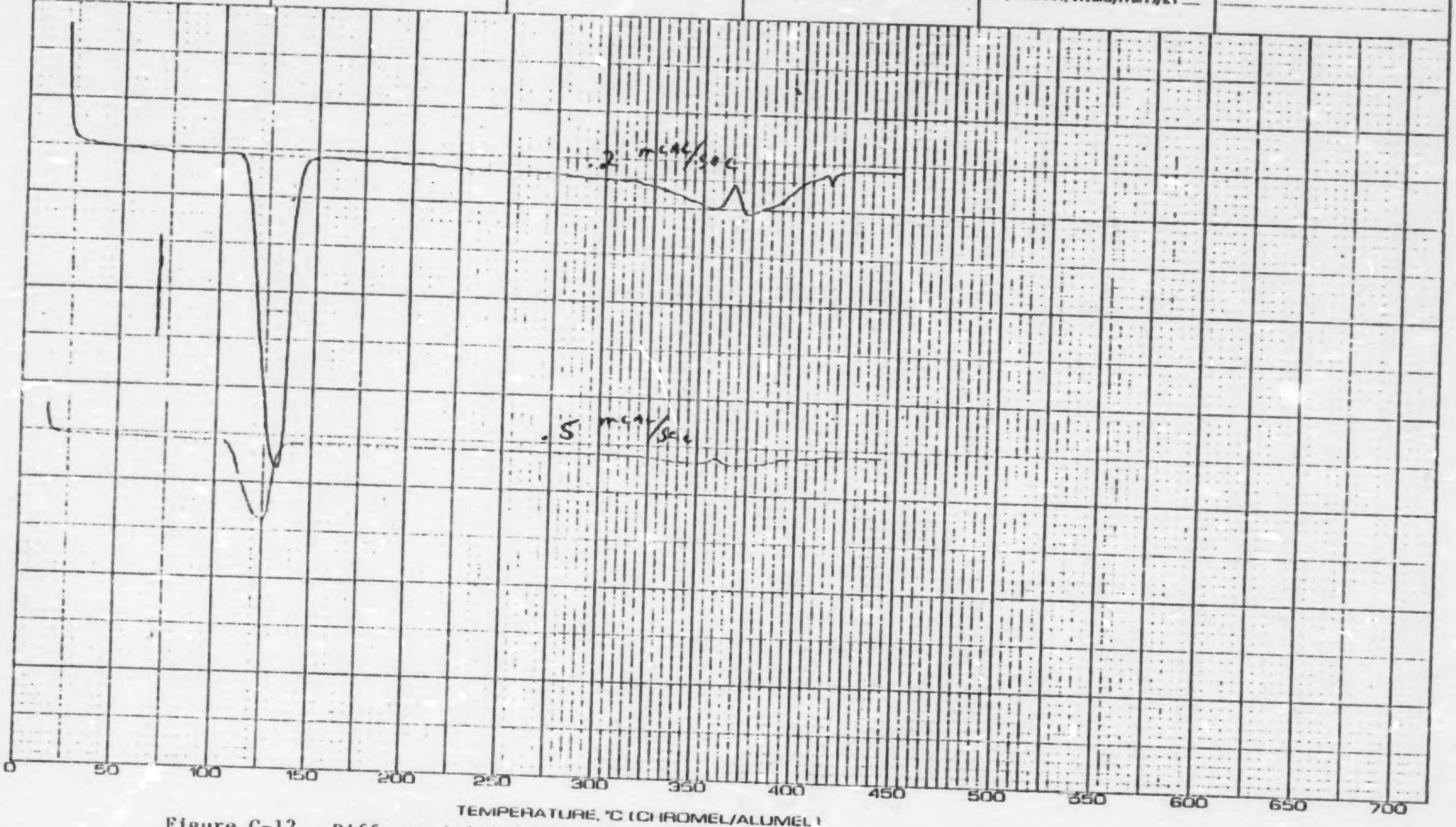


Figure G-12. Differential Calorimetry Scan of Solids Precipitated from Kinetic Run No. 40

PART NO. 990088

RUN NO 2 DATE 3/29/76
OPERATOR DLH
SAMPLE:
K-42 Run 42
ATM
FLOW RATE

T-AXIS
SCALE, °C/in 50
PROG. RATE, °C/min 10
HEAT ✓ COOL ISO
SHIFT, in. 0

DTA-DSC
SCALE, °C/in
(mcal/sec)/in
WEIGHT, mg 2.40
REFERENCE

TGA
SCALE, mg/in
SUPPRESSION, mg
WEIGHT, mg
TIME CONST., sec
dY, (mg/min)/in

TMA
SCALE, mils/in
MODE 6.02
SAMPLE SIZE 1.17
LOAD, g 7.19
dY, (10X), (mils/min)/in

C.L - Mg

X_{sol} = .16

mcal/sec	cm²	[illegible]	[illegible]
.5	4.9	2.49	.46
.2	2.8	.95	1.05

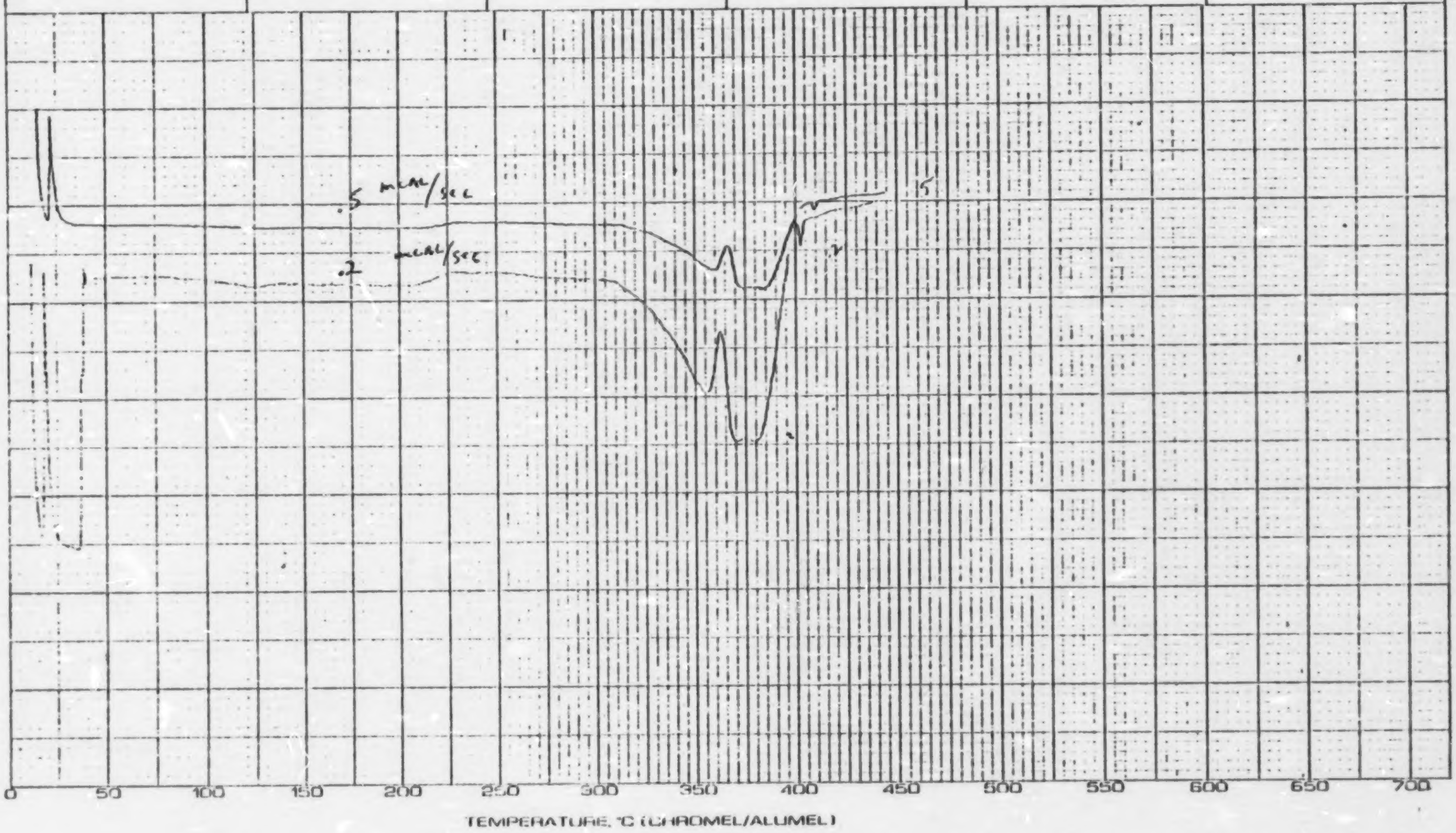
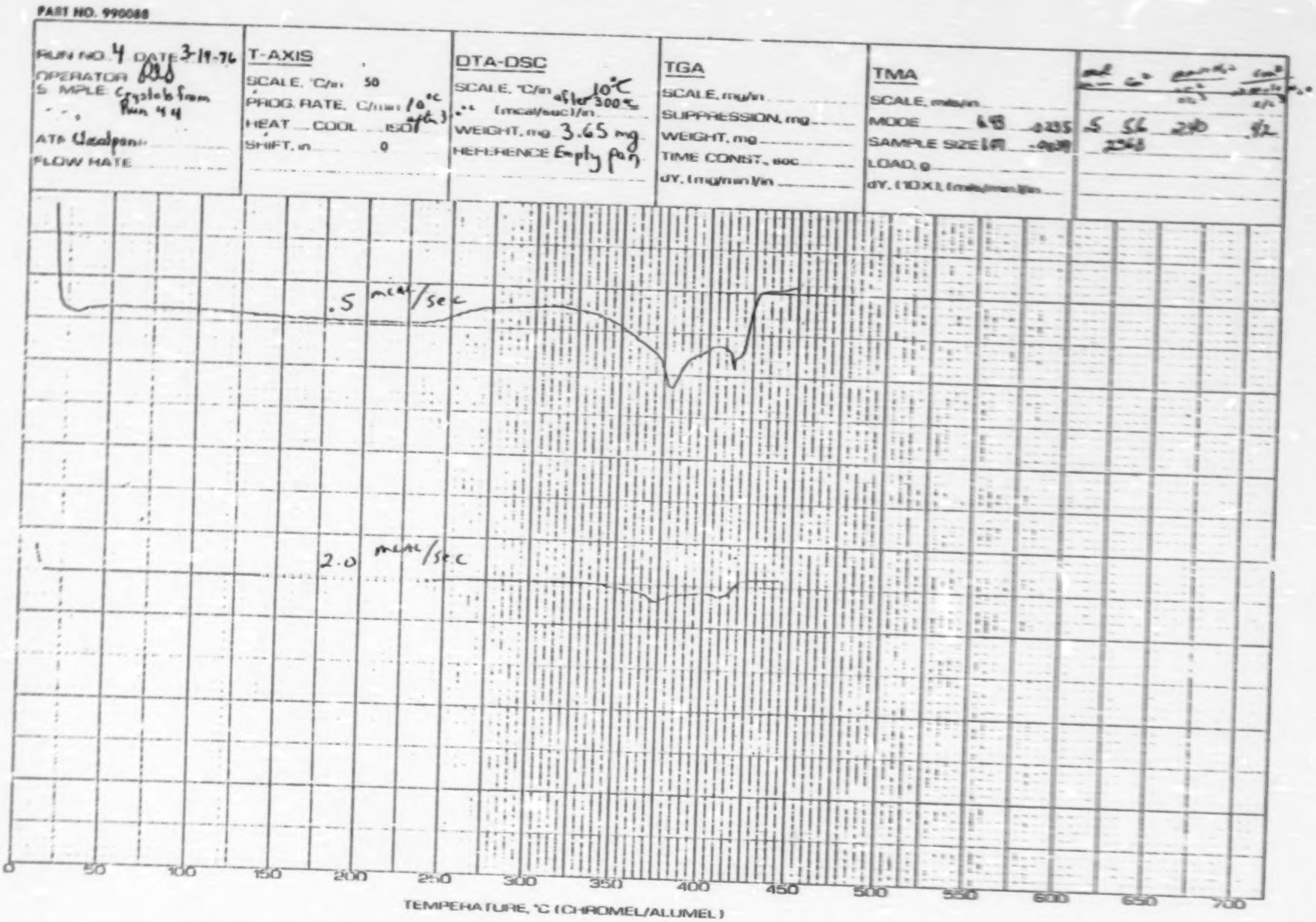


Figure C-13. Differential Calorimetry Scan of Solids Precipitated from Kinetic Run No. 42



PART NO. 990088

RUN NO. 4 DATE 3-19-76
OPERATOR [illegible]
SAMPLE Crystals from Run 44
ATM [illegible]
FLOW RATE

T-AXIS
SCALE, °C/in 50
PROG. RATE, °C/min 10 °C
HEAT COOL ISOT after 3)
SHIFT, in 0

DTA-DSC
SCALE, °C/in 10°C after 300°C
(mcal/sec)/in
WEIGHT, mg 3.65 mg
REFERENCE Empty pan

TGA
SCALE, mg/in
SUPPRESSION, mg
WEIGHT, mg
TIME CONST., sec
dY, (mg/min)/in

TMA
SCALE, mils/in
MODE [illegible]
SAMPLE SIZE [illegible]
LOAD, g
dY, (10X), (mils/min)/in

[illegible]

Figure C-14. Differential Calorimetry Scan of Solids Precipitated from Kinetic Run No. 44

PART NO. 990088

RUN NO 3 DATE 3/29/76
OPERATOR BF 8
SAMPLE Run 46
ATM
FLOW RATE

T-AXIS
SCALE, °C/in 50
PROG RATE, °C/min 10
HEAT & COOL 180
SHIFT, in 0

DTA-DSC
SCALE, °C/in 50
(mcal/sec)/in
WEIGHT, mg 3.00
REFERENCE
30°C

TGA
SCALE, mg/in
SUPPRESSION, mg
WEIGHT, mg
TIME CONST, sec
dY, (mg/min)/in

TMA
SCALE, mils/in
MODE 133
SAMPLE SIZE 101
LOAD, g
dY, (10X), (mils/min)/in

5 98 232
.1 243 46

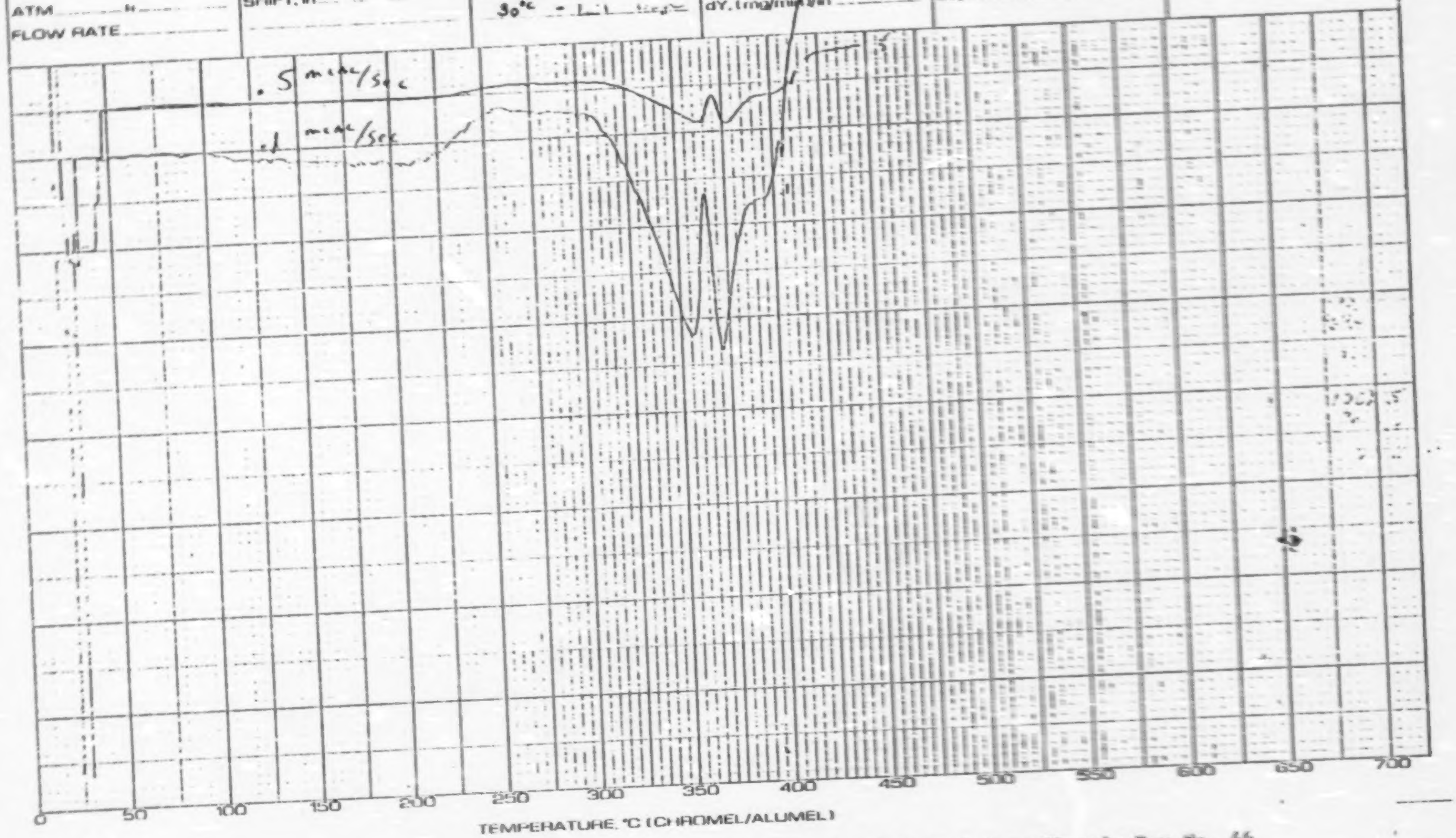
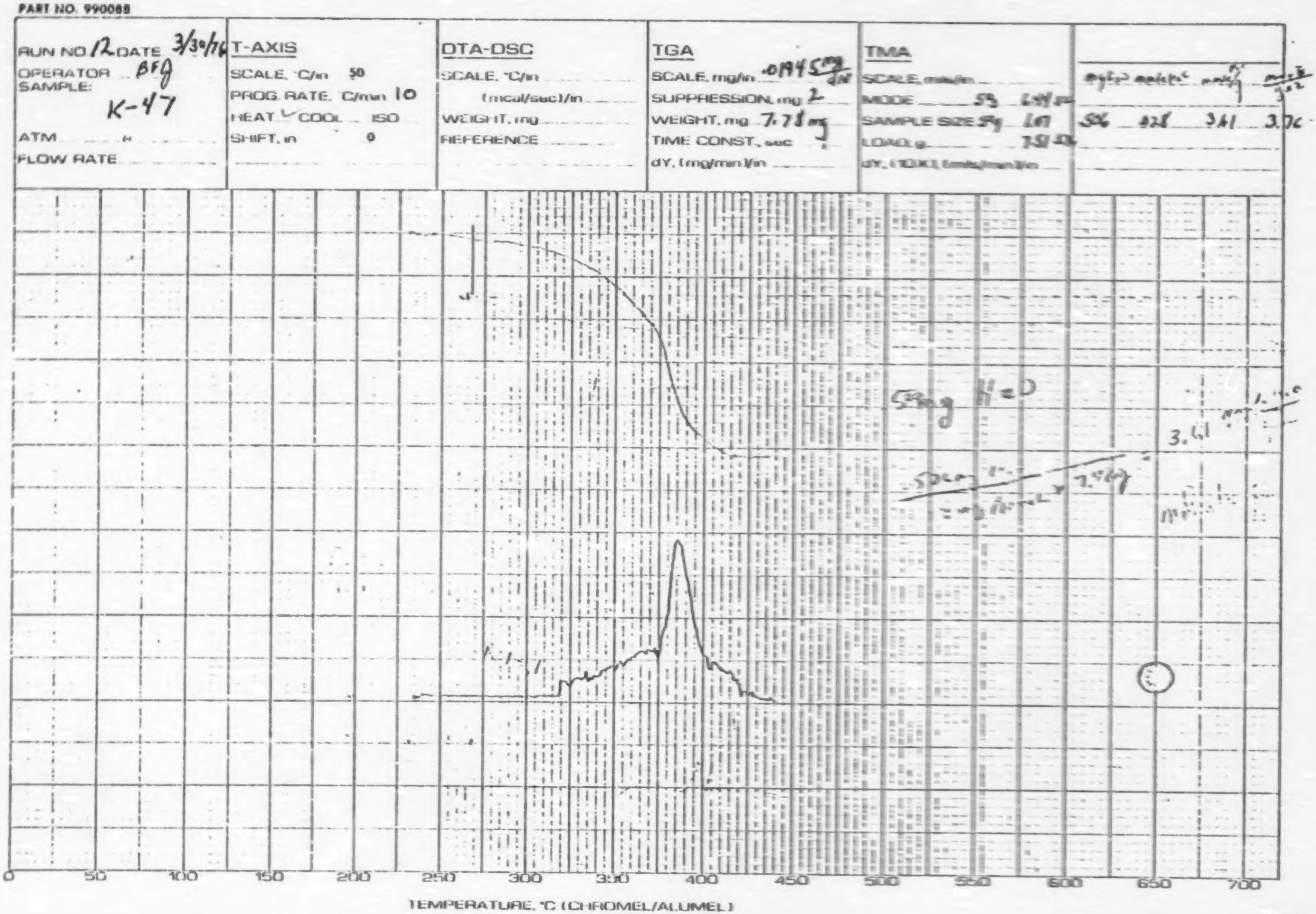


Figure G-15. Differential Calorimetry Scan of Solids Precipitated from Kinetic Run No. 46



PART NO. 990088

RUN NO 12 DATE 3/30/76
OPERATOR BFG
SAMPLE: K-47
ATM "
FLOW RATE

T-AXIS
SCALE, °C/in 50
PROG. RATE, °C/min 10
HEAT ✓ COOL ISO
SHIFT, in 0

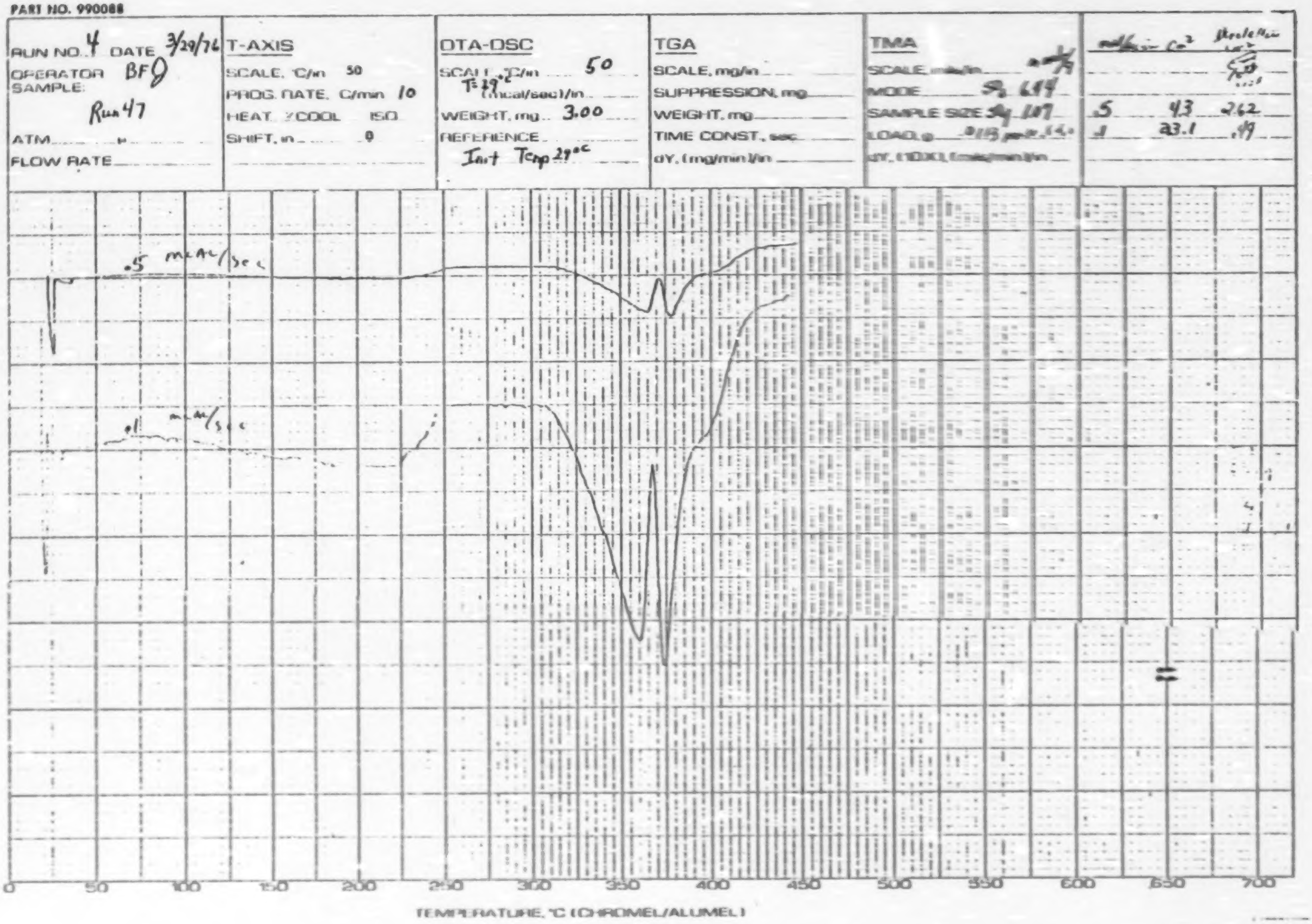
DTA-DSC
SCALE, °C/in
(mcal/sec)/in
WEIGHT, mg
REFERENCE

TGA
SCALE, mg/in .01945 mg/div
SUPPRESSION, mg 2
WEIGHT, mg 7.78 mg
TIME CONST., sec 1
dY, (mg/min)/in

TMA
SCALE, mils/in
MODE
SAMPLE SIZE
LOAD, g
dY, (10X1) (mils/min)/in

506 428 3.61 3.06

Figure G-16. Thermogravimetric Analysis of Solids Precipitated from Kinetic Run No. 47



PART NO. 990088

RUN NO. 4 DATE 3/29/76
OPERATOR BFJ
SAMPLE:
Run 47
ATM
FLOW RATE

T-AXIS
SCALE, °C/in 50
PROG. RATE, °C/min 10
HEAT, COOL ISO
SHIFT, in 0

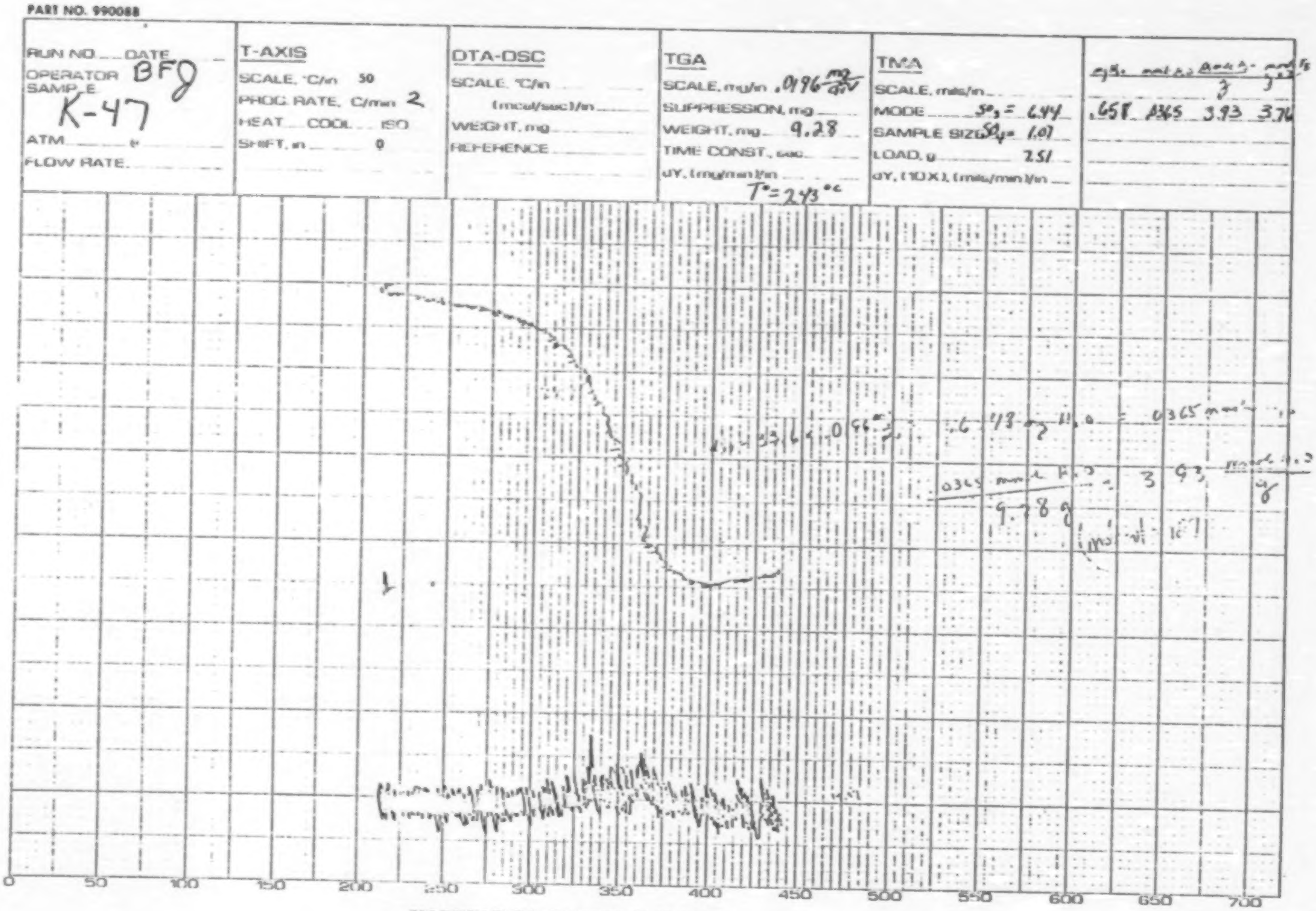
DTA-DSC
SCALE, °C/in 50
T=29°C (mcal/sec)/in
WEIGHT, mg 3.00
REFERENCE
Init Temp 29°C

TGA
SCALE, mg/in
SUPPRESSION, mg
WEIGHT, mg
TIME CONST., sec
dY, (mg/min)/in

TMA
SCALE, mils/in
MODE
SAMPLE SIZE
LOAD, g
dY, (10X), (mils/min)/in

.5 4.3 2.62
.1 23.1 .49

Figure C-17. Differential Calorimetry Scan of Solids Precipitated from Kinetic Run No. 47



RUN NO. ___ DATE ___
OPERATOR BFJ
SAMPLE K-47
ATM ___ ___
FLOW RATE ___

T-AXIS
SCALE, °C/in 50
PROG. RATE, C/min 2
HEAT ___ COOL ___ ISO
SHIFT, in ___ 0

DTA-DSC
SCALE, °C/in ___
(mcal/sec)/in ___
WEIGHT, mg ___
REFERENCE ___

TGA
SCALE, mg/in .0196 mg/div
SUPPRESSION, mg ___
WEIGHT, mg 9.28
TIME CONST., sec ___
dY, (mg/min)/in ___
T° = 243 °C

TMA
SCALE, mils/in ___
MODE ___ SO_3 = 6.44
SAMPLE SIZE SO_4 = 1.07
LOAD, g 2.51
dY, (10X), (mils/min)/in ___

.658 .0365 3.93 3.76

.6 48 mg H_2O = .0365 mmol

$$\frac{.0365\ \text{mmol}\ H_2O}{9.28\ g} = 3.93\ \frac{\text{mmol}}{g}$$

1
0
50
100
150
200
250
300
350
400
450
500
550
600
650
700
TEMPERATURE, °C (CHROMEL/ALUMEL)

Figure C-18. Thermogravimetric Analysis of Solids Precipitated from Kinetic Run No. 47

PART NO. 990088

RUN NO 5 DATE 3/29/74
OPERATOR BFG
SAMPLE Run 48
ATM
FLOW RATE

T-AXIS
SCALE, °C/in 50
PROG. RATE, °C/min
HEAT COOL ISO
SHIFT, in 0

DTA-DSC
SCALE, °C/in
(mcal/sec)/in
WEIGHT, mg 3.15
REFERENCE
Init temp 30 °C

TGA
SCALE, mg/in
SUPPRESSION, mg
WEIGHT, mg
TIME CONST., sec
dY, (mg/min)/in

TMA
SCALE, mils/in
MODE 617
SAMPLE SIZE 1.16 ÷ .09
LOAD, g corrected ÷ .15
dY, (10X), (mils/min)/in

mcal/sec	cm²	mcal·sec/sec
.5	4.1	2.18

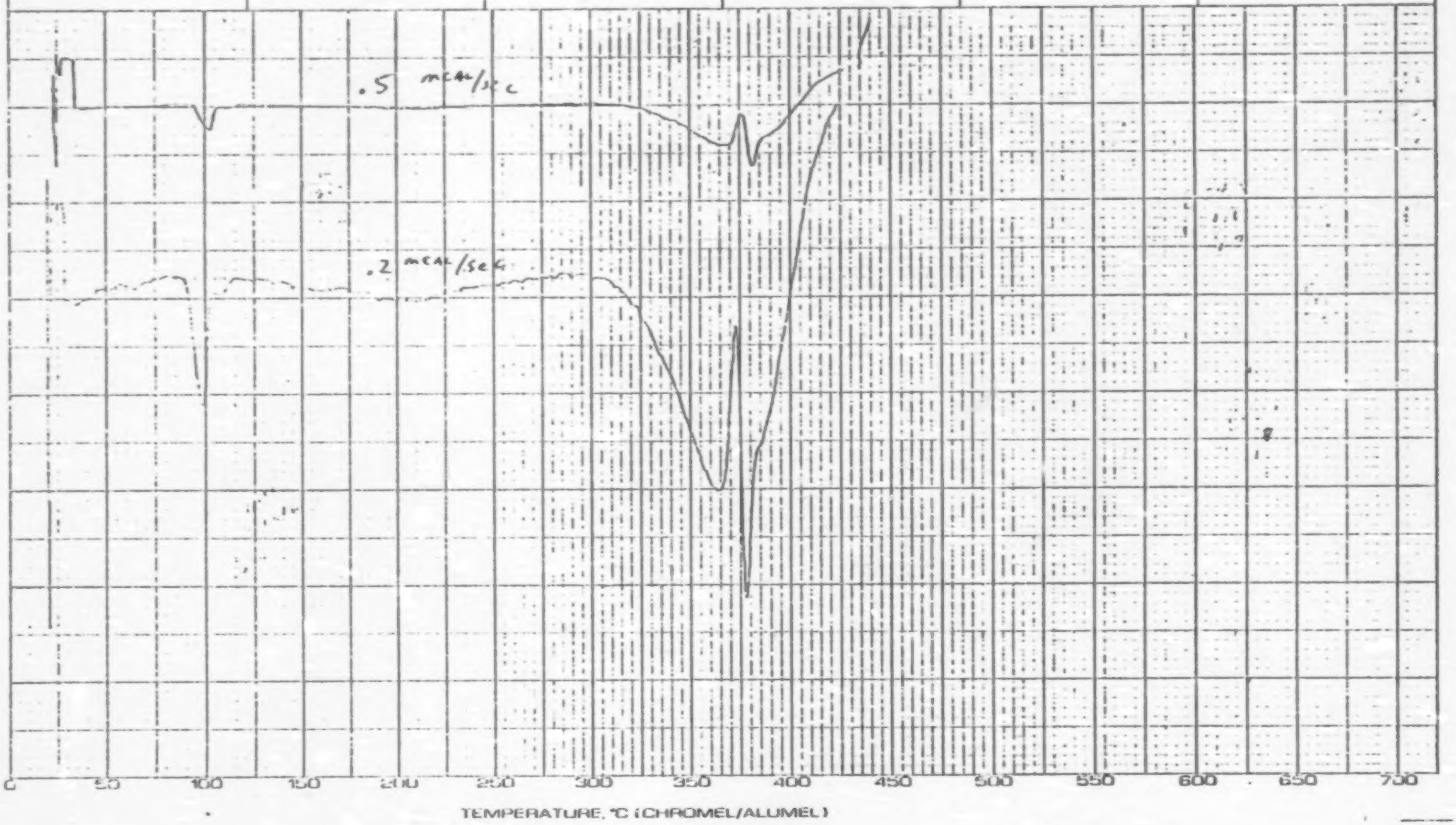
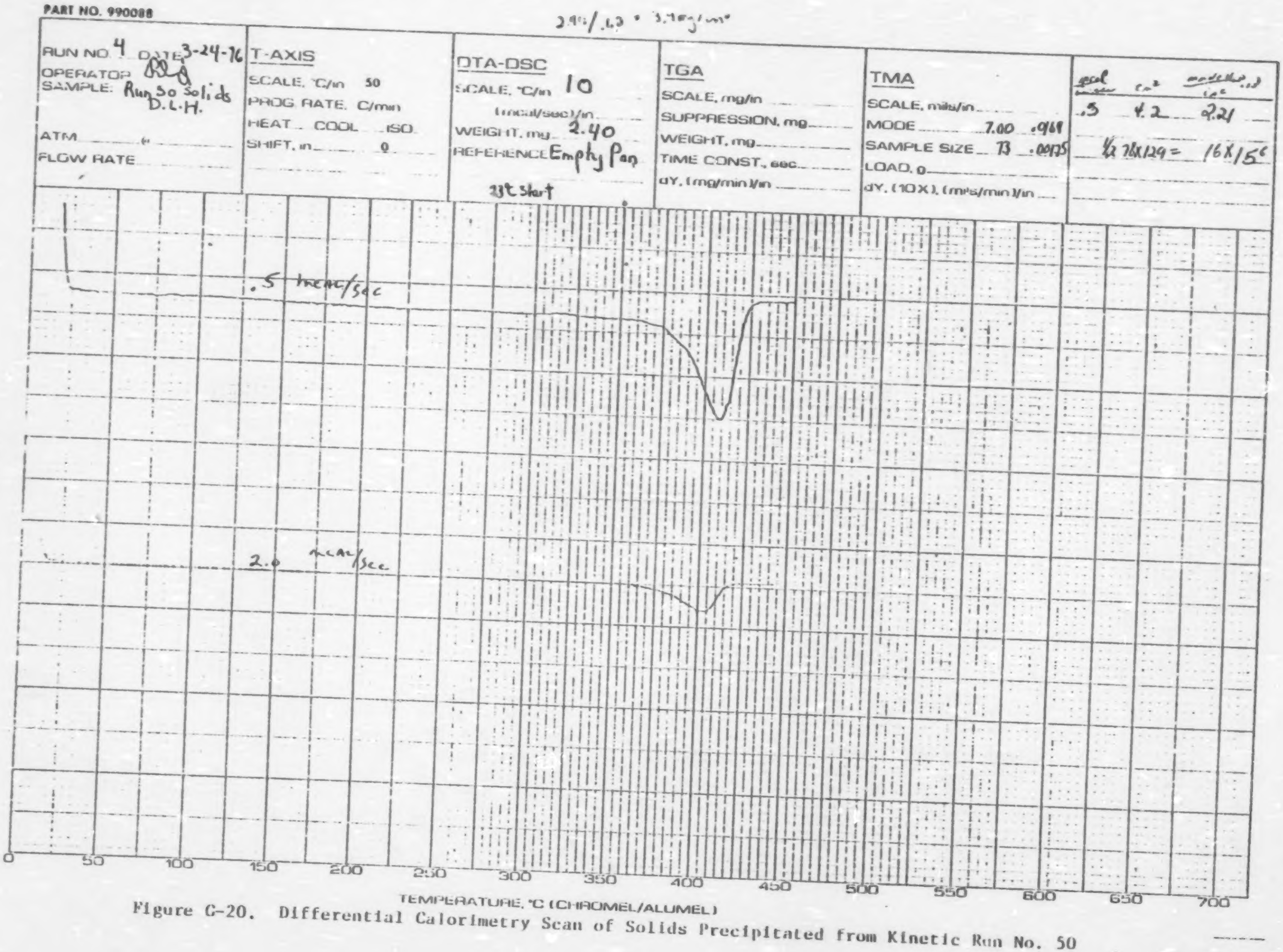


Figure G-19. Differential Calorimetry Scan of Solids Precipitated from Kinetic Run No. 48



PART NO. 990088

2.40/.63 = 3.4mg/in²

RUN NO. 4 DATE 3-24-76
OPERATOR
SAMPLE: Run 50 solids D.L.H.
ATM
FLOW RATE

T-AXIS
SCALE, °C/in 50
PROG RATE, C/min
HEAT COOL ISO
SHIFT, in 0

DTA-DSC
SCALE, °C/in 10
(mcal/sec)/in
WEIGHT, mg 2.40
REFERENCE Empty Pan

TGA
SCALE, mg/in
SUPPRESSION, mg
WEIGHT, mg
TIME CONST., sec
dY, (mg/min)/in

TMA
SCALE, mils/in
MODE 7.00 .969
SAMPLE SIZE 73 .00175
LOAD, g
dY, (10X), (mils/min)/in

mcal/sec	cm²	mcal/sec, s/cm²
.5	4.2	2.21

½ 78x129 = 16X/5°

23°C Start
.5 mcal/sec
2.0 mcal/sec
0
50
100
150
200
250
300
350
400
450
500
550
600
650
700
TEMPERATURE, °C (CHROMEL/ALUMEL)

Figure C-20. Differential Calorimetry Scan of Solids Precipitated from Kinetic Run No. 50

PART NO. 990088

RUN NO. 8 DATE 3/30/76
OPERATOR BFJ
SAMPLE: K-52
ATM
FLOW RATE

T-AXIS
SCALE, °C/in 50
PROG. RATE, °C/min 10
HEAT ✓ COOL 180
SHIFT, in 0

DTA-DSC
SCALE, °C/in 50
(mcal/sec)/in
WEIGHT, mg 2.89
REFERENCE
$T_0 = 49°$

TGA
SCALE, mg/in
SUPPRESSION, mg
WEIGHT, mg
TIME CONST., sec
dY, (mg/min)/in

TMA
SCALE, mils/in
MODE SO_3 6.62
SAMPLE SIZE SO_4 .10
LOAD, g
dY, (10X), (mils/min)/in

mcal / sec · cm² · mcal·g / [illegible]
5 4.6 2.33

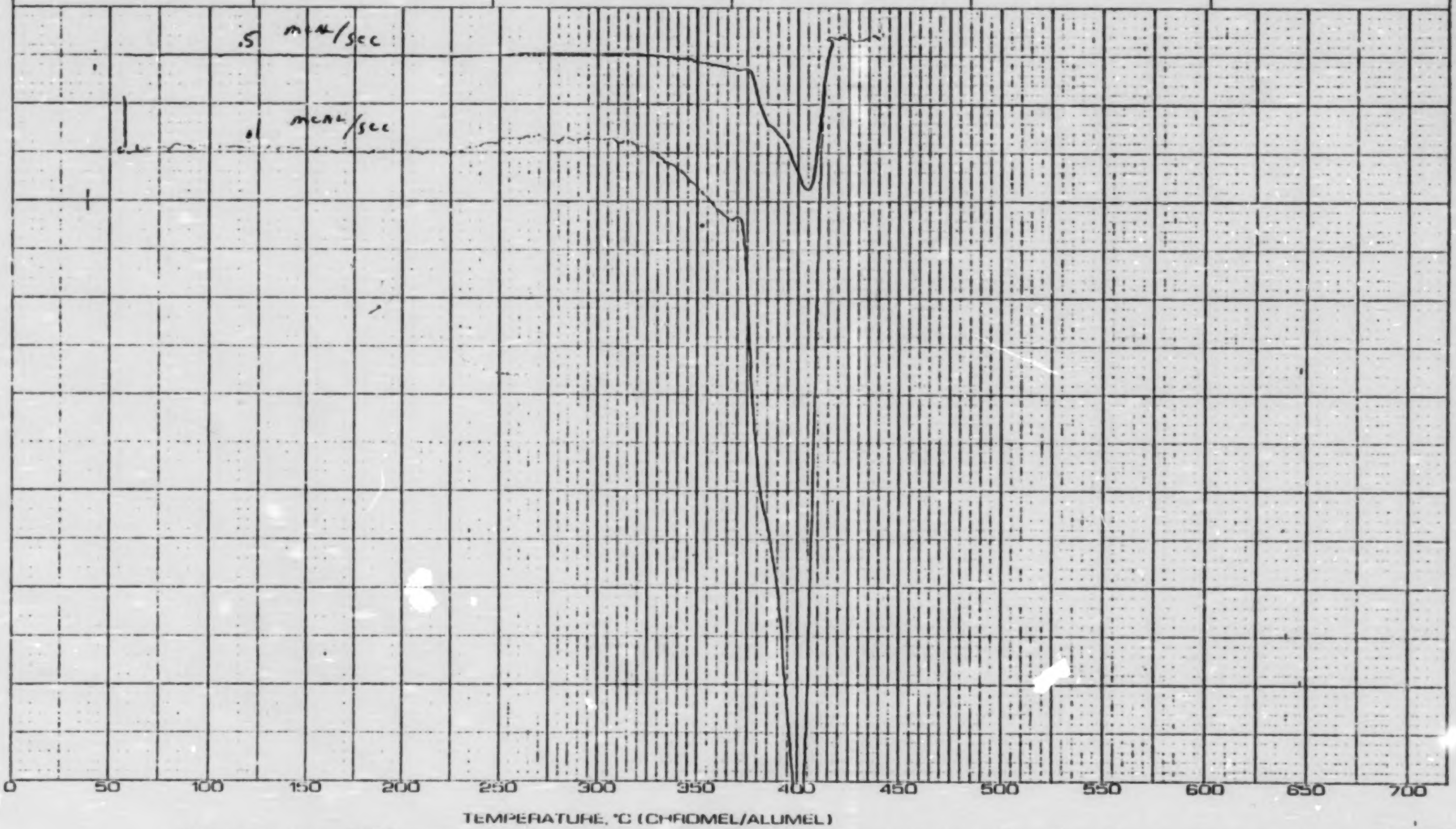


Figure G-21. Differential Calorimetry Scan of Solids Precipitated from Kinetic Run No. 52

PART NO. 990088

RUN NO. 1 DATE
OPERATOR B F g
SAMPLE: K-53
ATM
FLOW RATE

T-AXIS
SCALE, °C/in 50
PROG RATE, C/min 10
HEAT ✓ COOL 150
SHIFT, in 0

DTA-DSC
SCALE, °C/in 50
(mcal/sec)/in
WEIGHT, mg 2.80mg
REFERENCE
Initial temp - 29°c

TGA
SCALE, mg/in
SUPPRESSION, mg
WEIGHT, mg
TIME CONST., sec
dY, (mg/min)/in

TMA
SCALE, mils/in
MODE 6.69
SAMPLE SIZE .84
LOAD, g
dY, (10 X), (mils/min)/in

.5 4.6 229

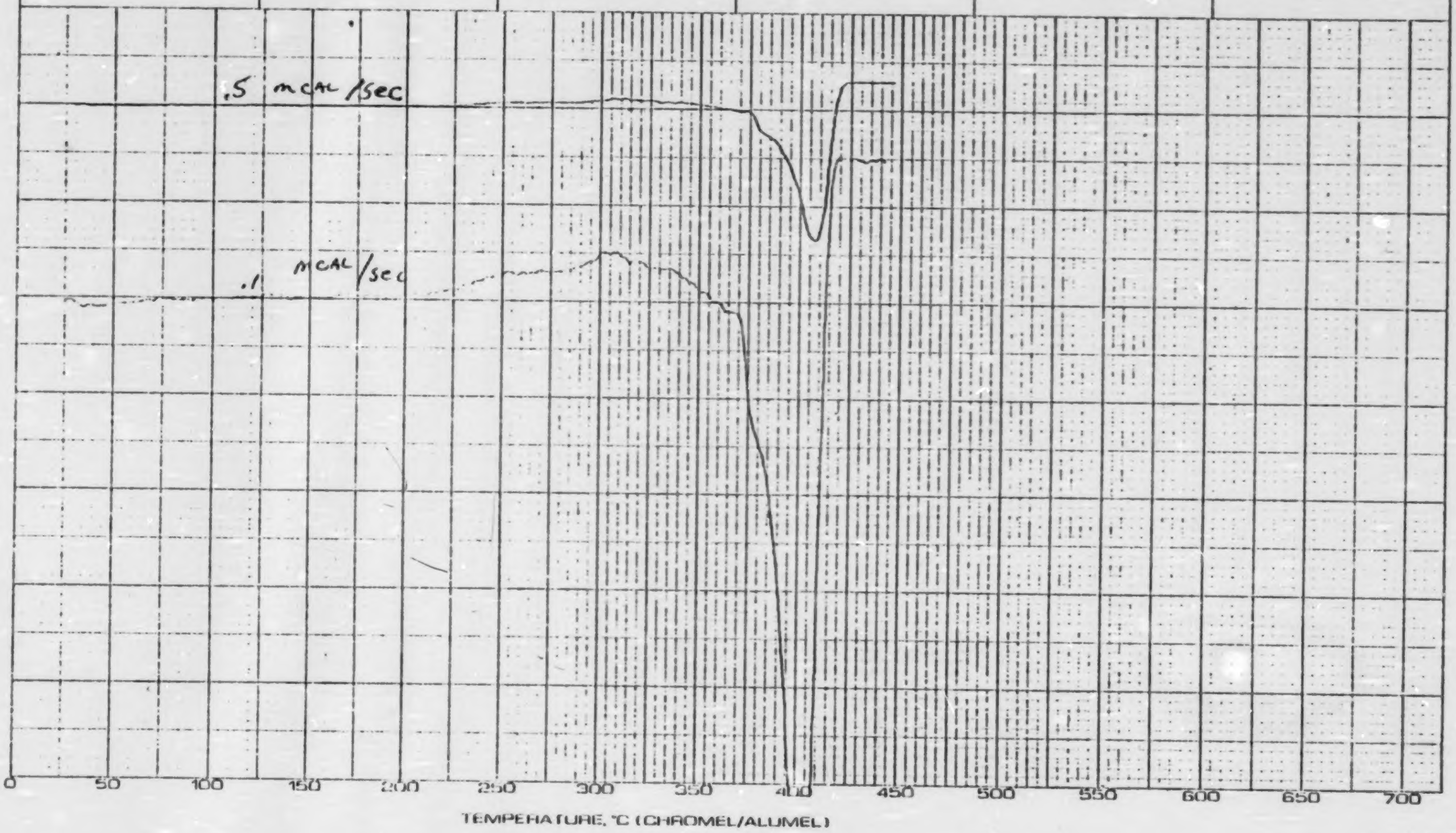
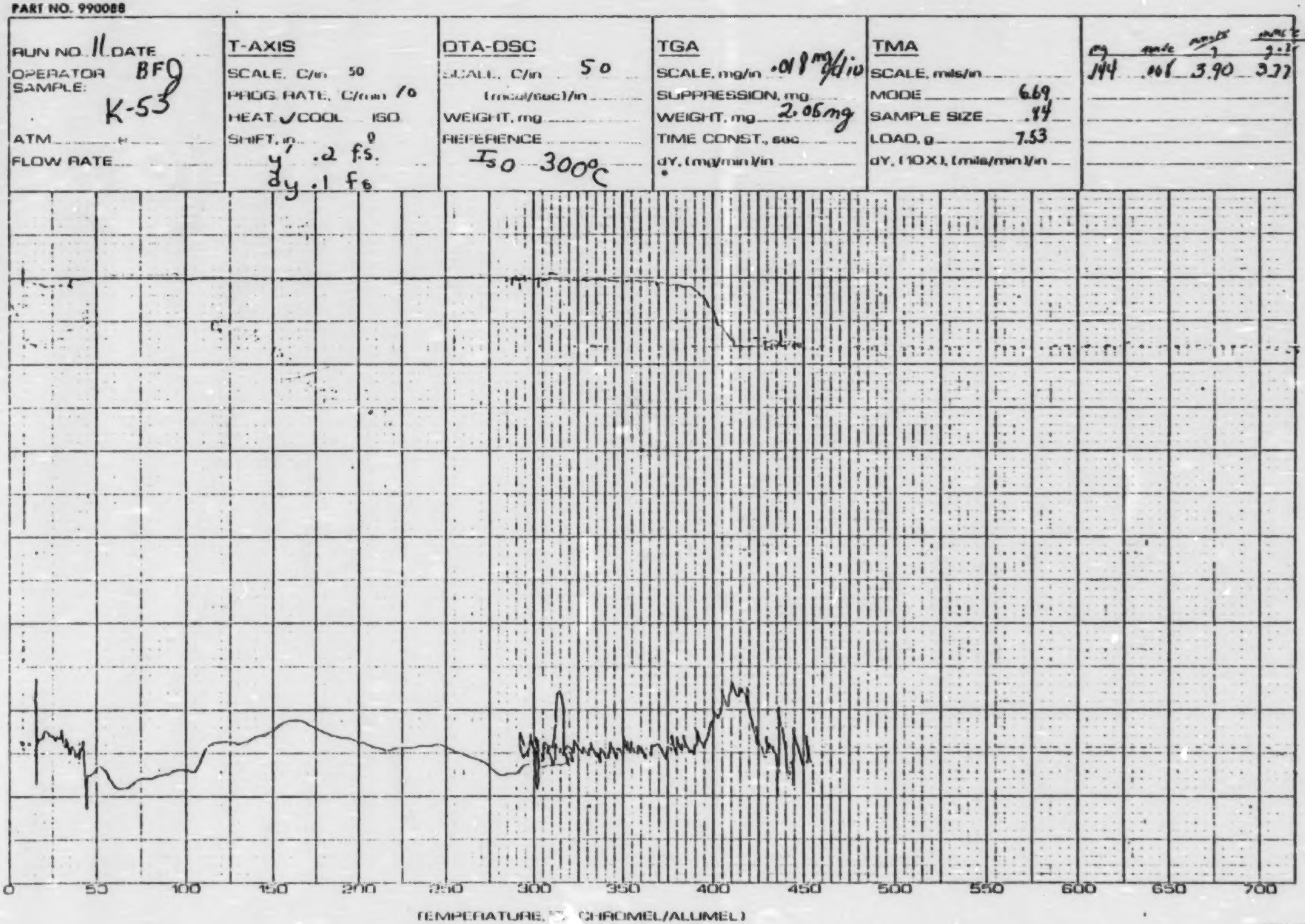


Figure G-22. Differential Calorimetry Scan of Solids Precipitated from Kinetic Run No. 53



PART NO. 990088

RUN NO. 11 DATE
OPERATOR BFG
SAMPLE: K-53
ATM
FLOW RATE

T-AXIS
SCALE, C/in 50
PROG RATE, C/min 10
HEAT ✓ COOL ISO
SHIFT, in 0
y' .2 f.s.
dy .1 fs

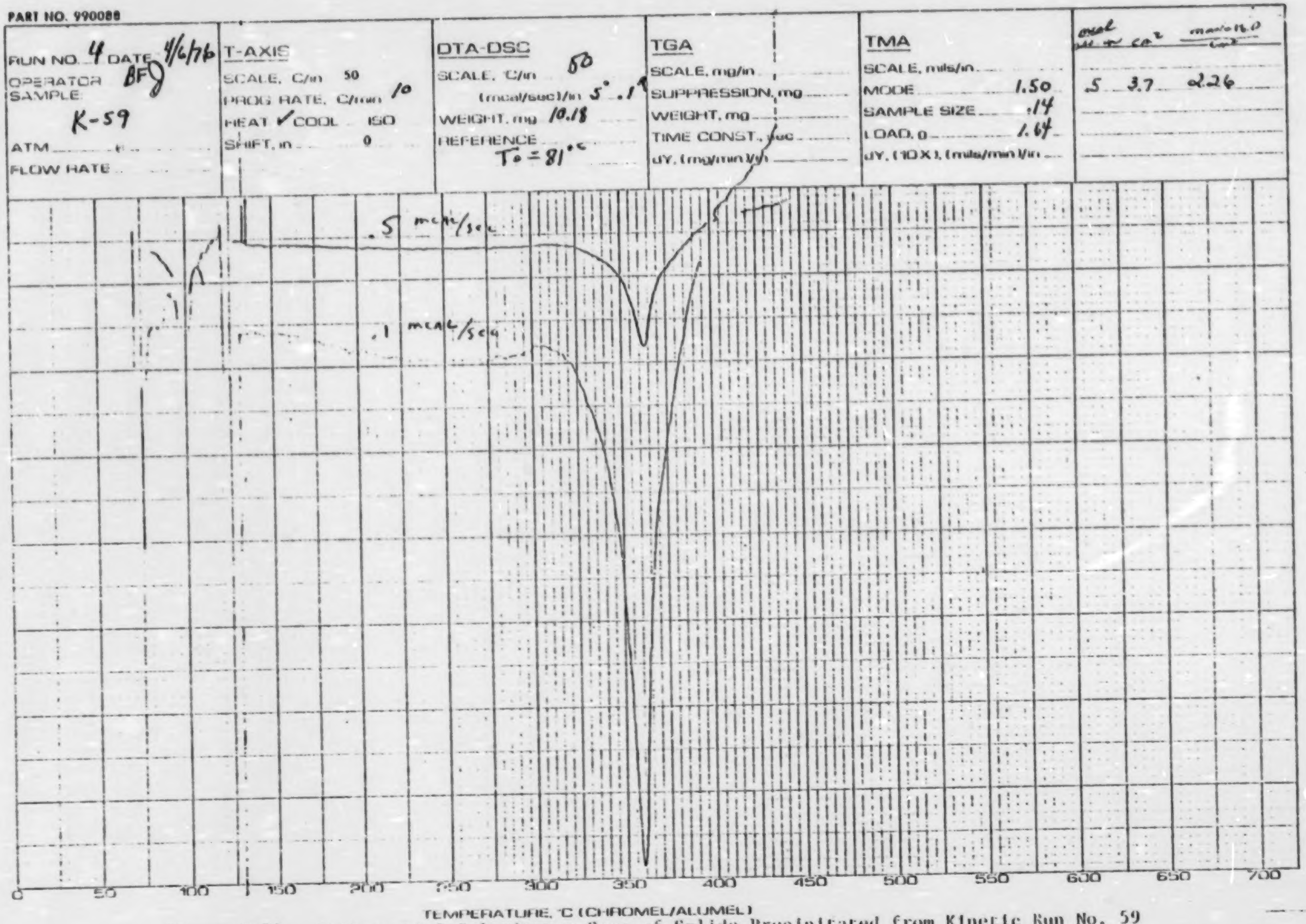
DTA-DSC
SCALE, C/in 50
(mcal/sec)/in
WEIGHT, mg
REFERENCE
Iso 300°C

TGA
SCALE, mg/in .018 mg/div
SUPPRESSION, mg
WEIGHT, mg 2.06 mg
TIME CONST., sec
dY, (mg/min)/in

TMA
SCALE, mils/in
MODE 6.69
SAMPLE SIZE .84
LOAD, g 7.53
dY, (10X), (mils/min)/in

mg	mole	[illegible]	[illegible]
.144	.001	3.90	3.77

Figure G-23. Thermogravimetric Analysis of Solids Precipitated from Kinetic Run No. 47



PART NO. 990088

RUN NO. 4 DATE 4/6/76
OPERATOR BFJ
SAMPLE K-59
ATM
FLOW RATE

T-AXIS
SCALE, C/in 50
PROG RATE, C/min 10
HEAT ✓ COOL ISO
SHIFT, in 0

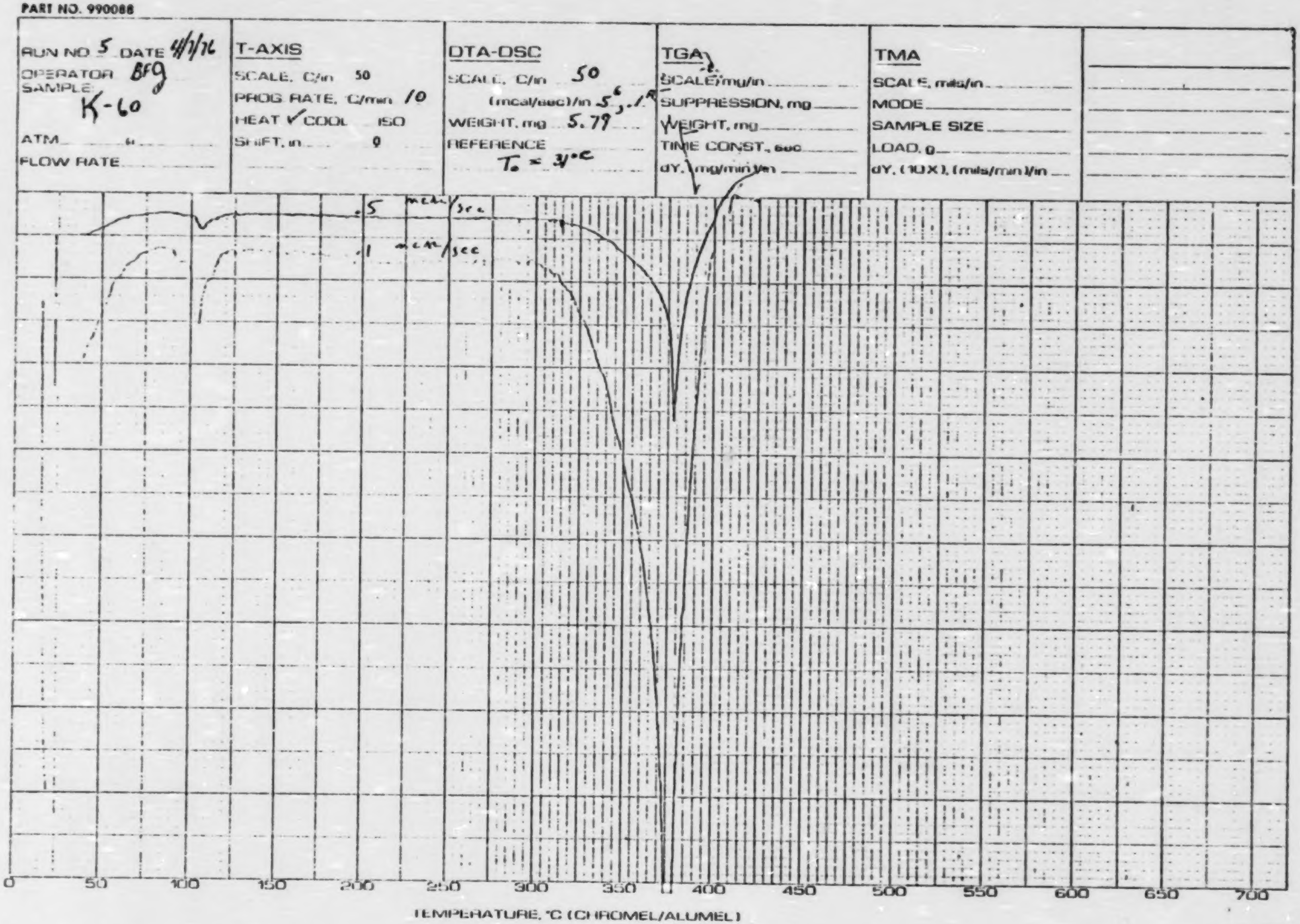
DTA-DSC
SCALE, C/in 50
(mcal/sec)/in 5° .1
WEIGHT, mg 10.18
REFERENCE
T₀ = 81°C

TGA
SCALE, mg/in
SUPPRESSION, mg
WEIGHT, mg
TIME CONST., sec
dY, (mg/min)/in

TMA
SCALE, mils/in
MODE 1.50
SAMPLE SIZE .14
LOAD, g 1.64
dY, (10X), (mils/min)/in

[illegible]
.5 3.7 2.26

Figure C-24. Differential Calorimetry Scan of Solids Precipitated from Kinetic Run No. 59



PART NO. 990088

RUN NO. 5 DATE 4/7/76
OPERATOR BFG
SAMPLE K-60
ATM
FLOW RATE

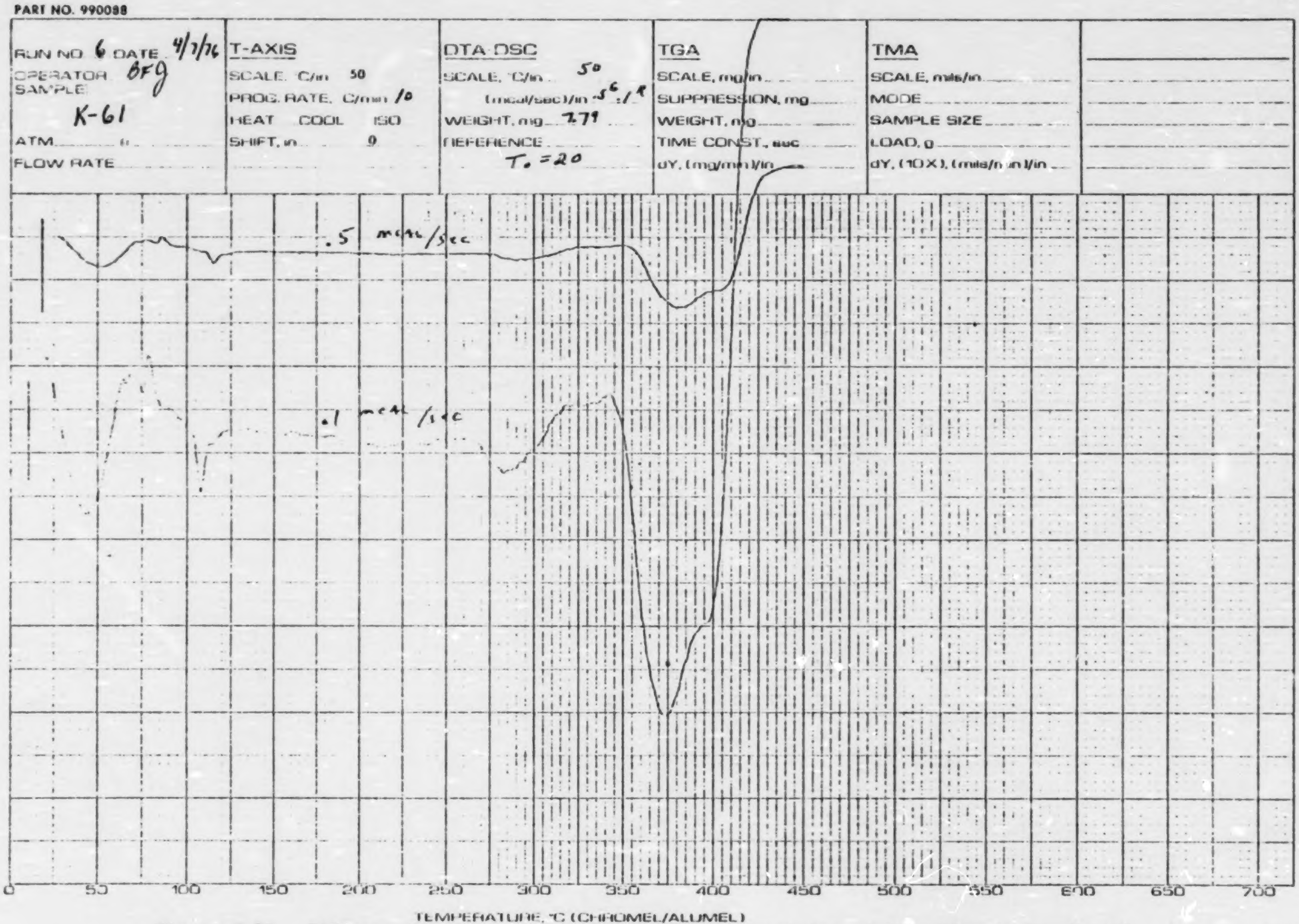
T-AXIS
SCALE, C/in 50
PROG RATE, C/min 10
HEAT ✓ COOL ISO
SHIFT, in 0

DTA-DSC
SCALE, C/in 50
(mcal/sec)/in .5, .1
WEIGHT, mg 5.79
REFERENCE
$T_o = 31°C$

TGA
SCALE, mg/in
SUPPRESSION, mg
WEIGHT, mg
TIME CONST, sec
dY, (mg/min)/in

TMA
SCALE, mils/in
MODE
SAMPLE SIZE
LOAD, g
dY, (10X), (mils/min)/in

Figure C-25. Differential Calorimetry Scan of Solids Precipitated from Kinetic Run No. 60



PART NO. 990098

RUN NO. 6 DATE 4/7/76
OPERATOR BFG
SAMPLE K-61
ATM ''
FLOW RATE

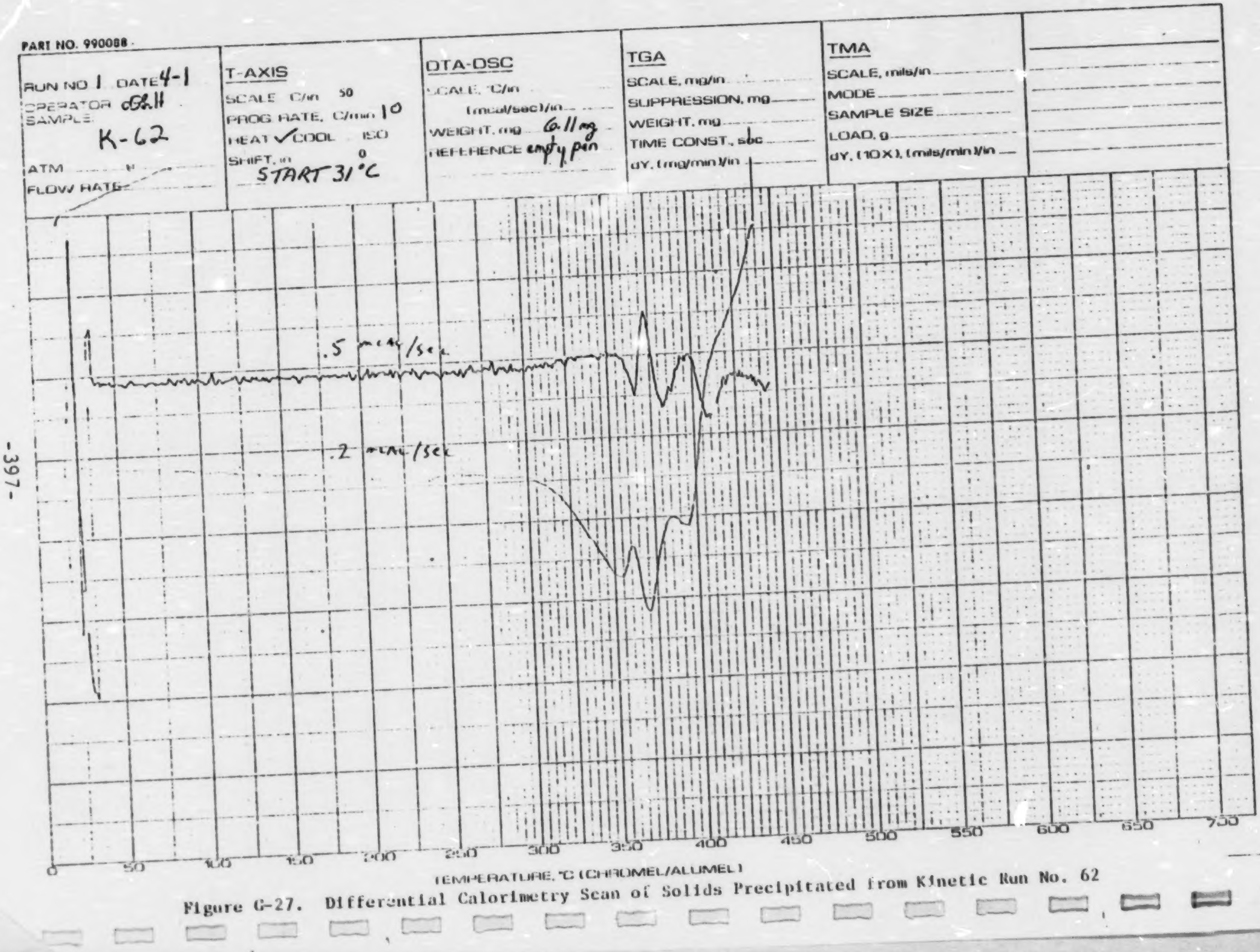
T-AXIS
SCALE, °C/in 50
PROG. RATE, °C/min 10
HEAT COOL 150
SHIFT, in 0

DTA-DSC
SCALE, °C/in 50
(mcal/sec)/in $.5^{6}$ $.1^{R}$
WEIGHT, mg 279
REFERENCE
$T_0 = 20$

TGA
SCALE, mg/in
SUPPRESSION, mg
WEIGHT, mg
TIME CONST, sec
dY, (mg/min)/in

TMA
SCALE, mils/in
MODE
SAMPLE SIZE
LOAD, g
dY, (10X), (mils/min)/in

Figure G-26. Differential Calorimetry Scan of Solids Precipitated from Kinetic Run No. 61



PART NO. 990088

RUN NO 1 DATE 4-1
OPERATOR [illegible]
SAMPLE: K-62
ATM
FLOW RATE

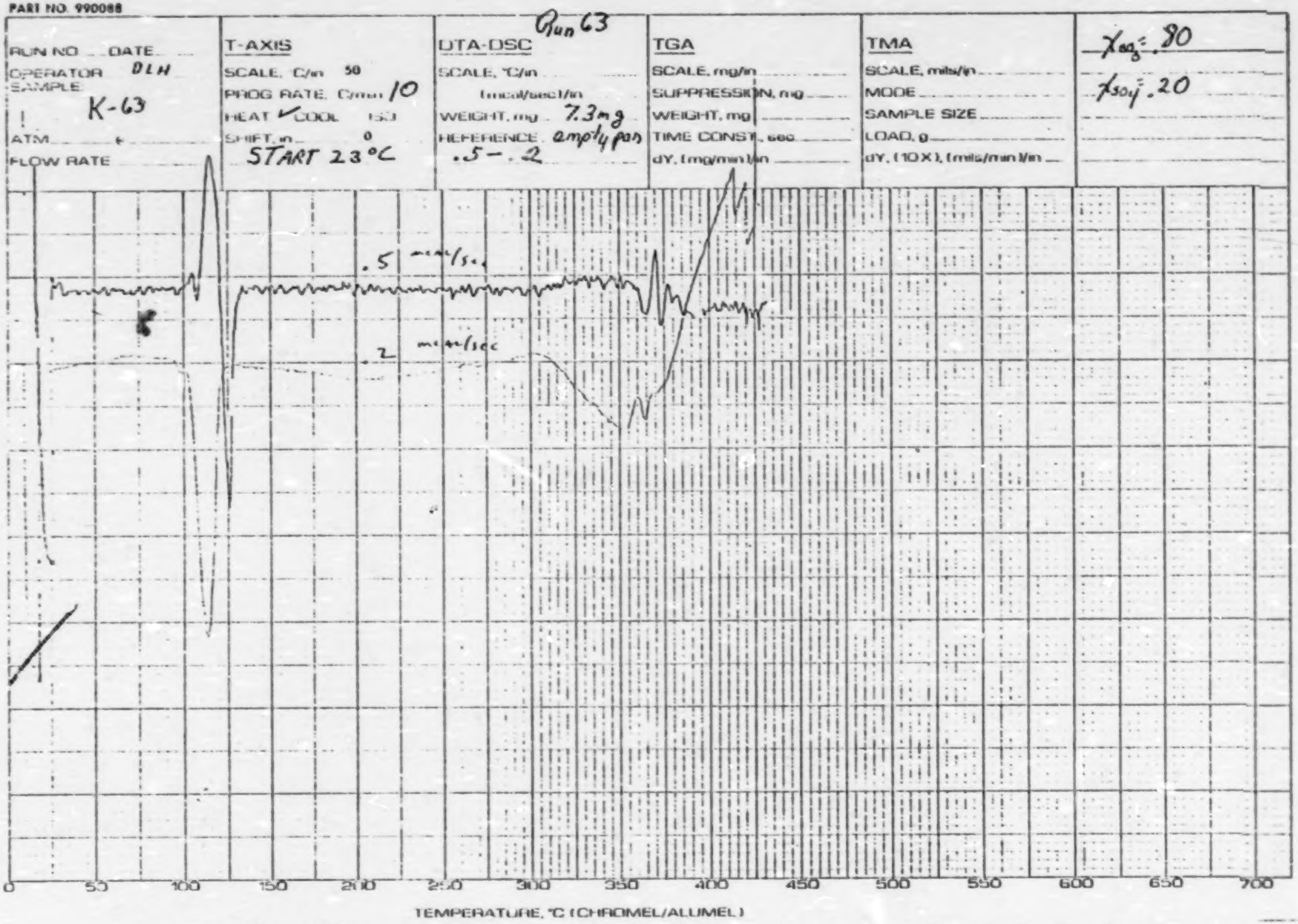
T-AXIS
SCALE C/in 50
PROG RATE, C/min 10
HEAT ✓ COOL 150
SHIFT, in 0
START 31°C

DTA-DSC
SCALE, °C/in
(mcal/sec)/in
WEIGHT, mg 6.11 mg
REFERENCE empty pan

TGA
SCALE, mg/in
SUPPRESSION, mg
WEIGHT, mg
TIME CONST, sec
dY, (mg/min)/in

TMA
SCALE, mils/in
MODE
SAMPLE SIZE
LOAD, g
dY, (10X), (mils/min)/in

Figure C-27. Differential Calorimetry Scan of Solids Precipitated from Kinetic Run No. 62



PART NO. 990088

RUN NO. DATE

OPERATOR DLH

SAMPLE K-63

ATM

FLOW RATE

T-AXIS

SCALE, C/in 50

PROG RATE, C/min 10

HEAT ✓ COOL 150

SHIFT, in 0

START 23°C

DTA-DSC Run 63

SCALE, °C/in

(mcal/sec)/in

WEIGHT, mg 7.3mg

REFERENCE empty pan

.5 - .2

TGA

SCALE, mg/in

SUPPRESSION, mg

WEIGHT, mg

TIME CONST, sec

dY, (mg/min)/in

TMA

SCALE, mils/in

MODE

SAMPLE SIZE

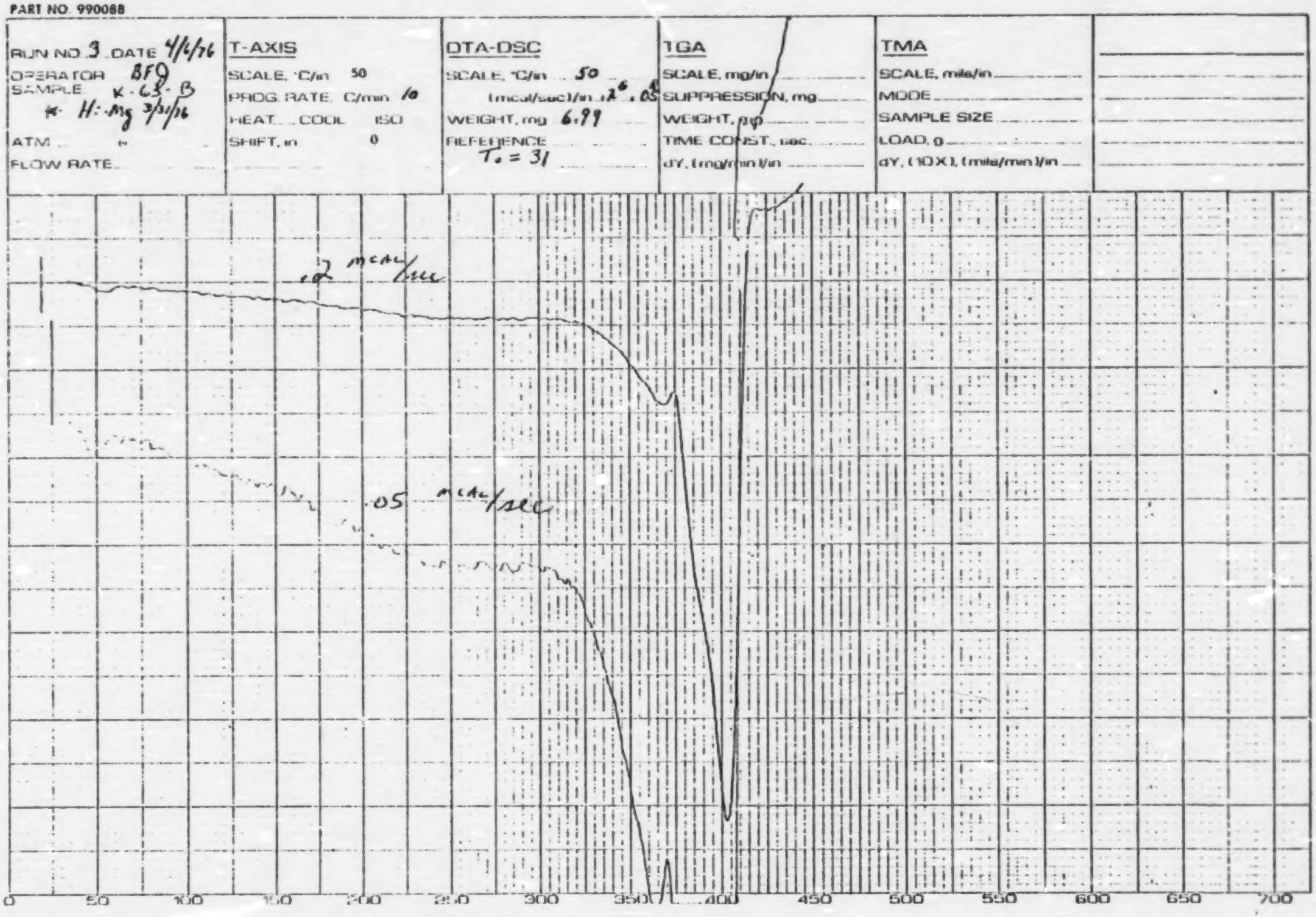
LOAD, g

dY, (10X), (mils/min)/in

X_{aq} = .80

X_{soy} = .20

Figure C-28. Differential Calorimetry Scan of Solids Precipitated from Kinetic Run No. 63



PART NO. 990088

RUN NO. 3 DATE 4/6/76
OPERATOR BFG
SAMPLE K-63-B
K- H:-Mg 3/31/76
ATM. ←
FLOW RATE

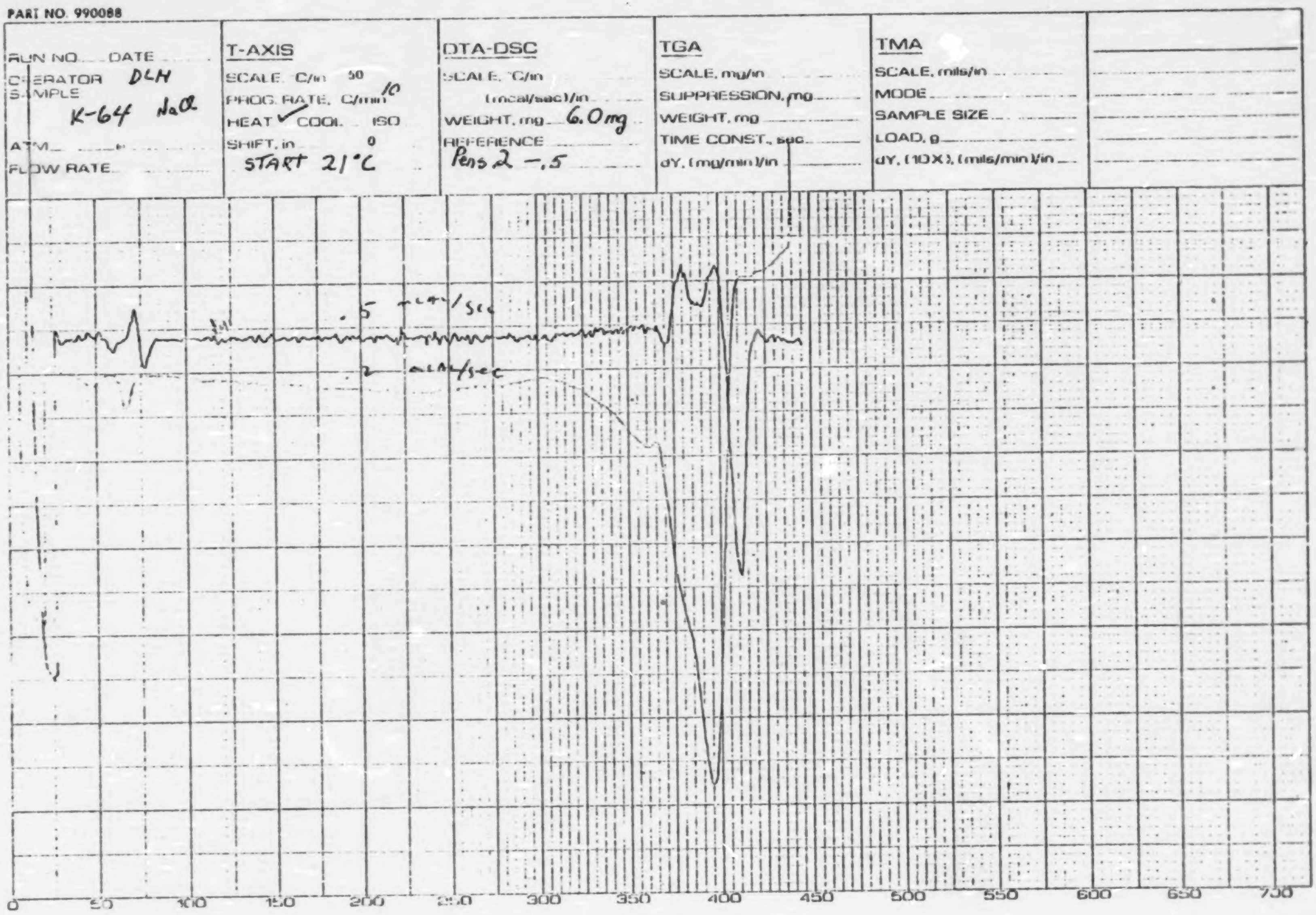
T-AXIS
SCALE, °C/in 50
PROG. RATE, C/min 10
HEAT ... COOL ISO
SHIFT, in 0

DTA-DSC
SCALE, °C/in 50
(mcal/sec)/in .2 .05
WEIGHT, mg 6.99
REFERENCE
$T_o = 31$

TGA
SCALE, mg/in
SUPPRESSION, mg
WEIGHT, mg
TIME CONST., sec
dY, (mg/min)/in

TMA
SCALE, mils/in
MODE
SAMPLE SIZE
LOAD, g
dY, (10X), (mils/min)/in

Figure C-29. Differential Calorimetry Scan of Solids Precipitated from Kinetic Run No. 63



PART NO. 990088

RUN NO. ___ DATE ___	**T-AXIS**	**DTA-DSC**	**TGA**	**TMA**	
OPERATOR DLH	SCALE, C/in 50	SCALE, °C/in ___	SCALE, mg/in ___	SCALE, mils/in ___	
SAMPLE K-64 NaCl	PROG. RATE, C/min 10	(mcal/sec)/in ___	SUPPRESSION, mg ___	MODE ___	
	HEAT ✓ COOL ISO	WEIGHT, mg 6.0mg	WEIGHT, mg ___	SAMPLE SIZE ___	
ATM ___	SHIFT, in 0	REFERENCE ___	TIME CONST., sec ___	LOAD, g ___	
FLOW RATE ___	START 21°C	Pens 2 -.5	dY, (mg/min)/in ___	dY, (10X), (mils/min)/in ___	

Figure G-30. Differential Calorimetry Scan of Solids Precipitated from Kinetic Run No. 64

PART NO. 990088

RUN NO ___ DATE 4/11/76
OPERATOR BFJ
SAMPLE: K-64
ATM ___
FLOW RATE ___

T-AXIS
SCALE, °C/in 50
PROG. RATE, C/min 10
HEAT COOL ISO
SHIFT, in 0

DTA-DSC
SCALE, °C/in 50
(mcal/sec)/in ___
WEIGHT, mg 6.27
REFERENCE To=24°C

TGA
SCALE, mg/in ___
SUPPRESSION, mg ___
WEIGHT, mg ___
TIME CONST., sec 1
dY, (mg/min)/in ___

TMA
SCALE, mils/in ___
MODE ___
SAMPLE SIZE ___
LOAD, g ___
dY, (10X), (mils/min)/in ___

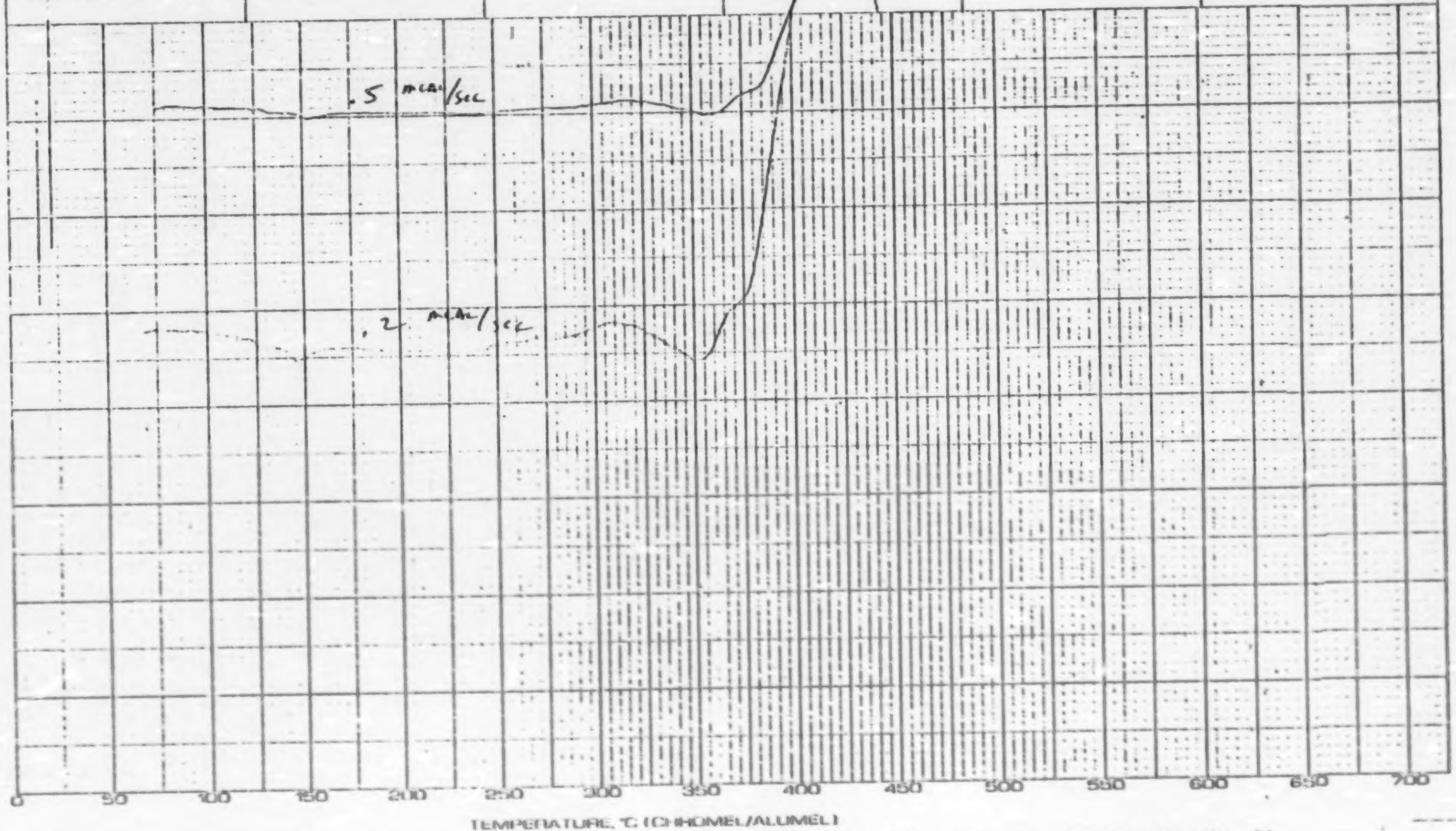


Figure G-31. Differential Calorimetry Scan of Solids Precipitated from Kinetic Run No. 64

PART NO. 990088

RUN NO 1 DATE 4/6/76	**T-AXIS**	**DTA-DSC**	**TGA**	**TMA**	
OPERATOR BFJ	SCALE, °C/in 50	SCALE, °C/in 50	SCALE, mg/in	SCALE, mils/in	.5 mg -LS.
SAMPLE K-65	PROG. RATE, C/min 10	(mcal/sec)/in .5	SUPPRESSION, mg	MODE	T= 55°C
ATM	HEAT✓ COOL ISO	WEIGHT, mg 17.17	WEIGHT, mg	SAMPLE SIZE	
FLOW RATE	SHIFT, in 0	REFERENCE	TIME CONST., sec	LOAD, g	
		$T_0 = 21°C$	dY, (mg/min)/in	dY, (10X), (mils/min)/in	

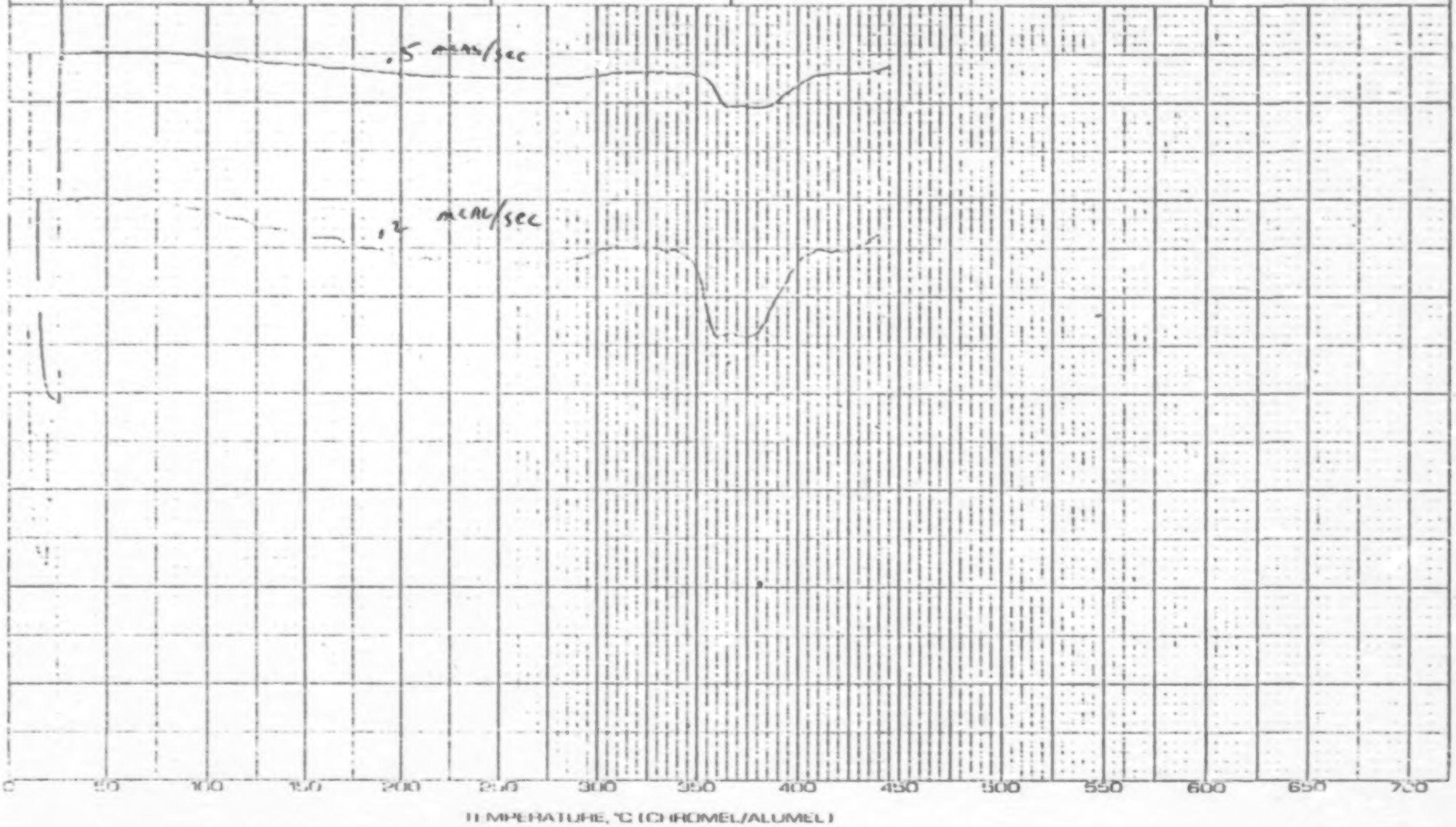


Figure G-32. Differential Calorimetry Scan of Solids Precipitated from Kinetic Run No. 65

PART NO. 990088

RUN NO 2 DATE 4/6/76
OPERATOR BFJ
SAMPLE K-66
ATM ________
FLOW RATE ________

T-AXIS
SCALE, °C/in 50
PROG. RATE, C/min 10
HEAT ✓ COOL 150
SHIFT, in 0

DTA-DSC
SCALE, °C/in 50
(mcal/sec)/in .2, .1
WEIGHT, mg 10.74
REFERENCE
T_0 = 4/1 °C

TGA
SCALE, mg/in ________
SUPPRESSION, mg ________
WEIGHT, mg ________
TIME CONST., sec ________
dY, (mg/min)/in ________

TMA
SCALE, mils/in ________
MODE ________
SAMPLE SIZE ________
LOAD, g ________
dY, (10X), (mils/min)/in ________

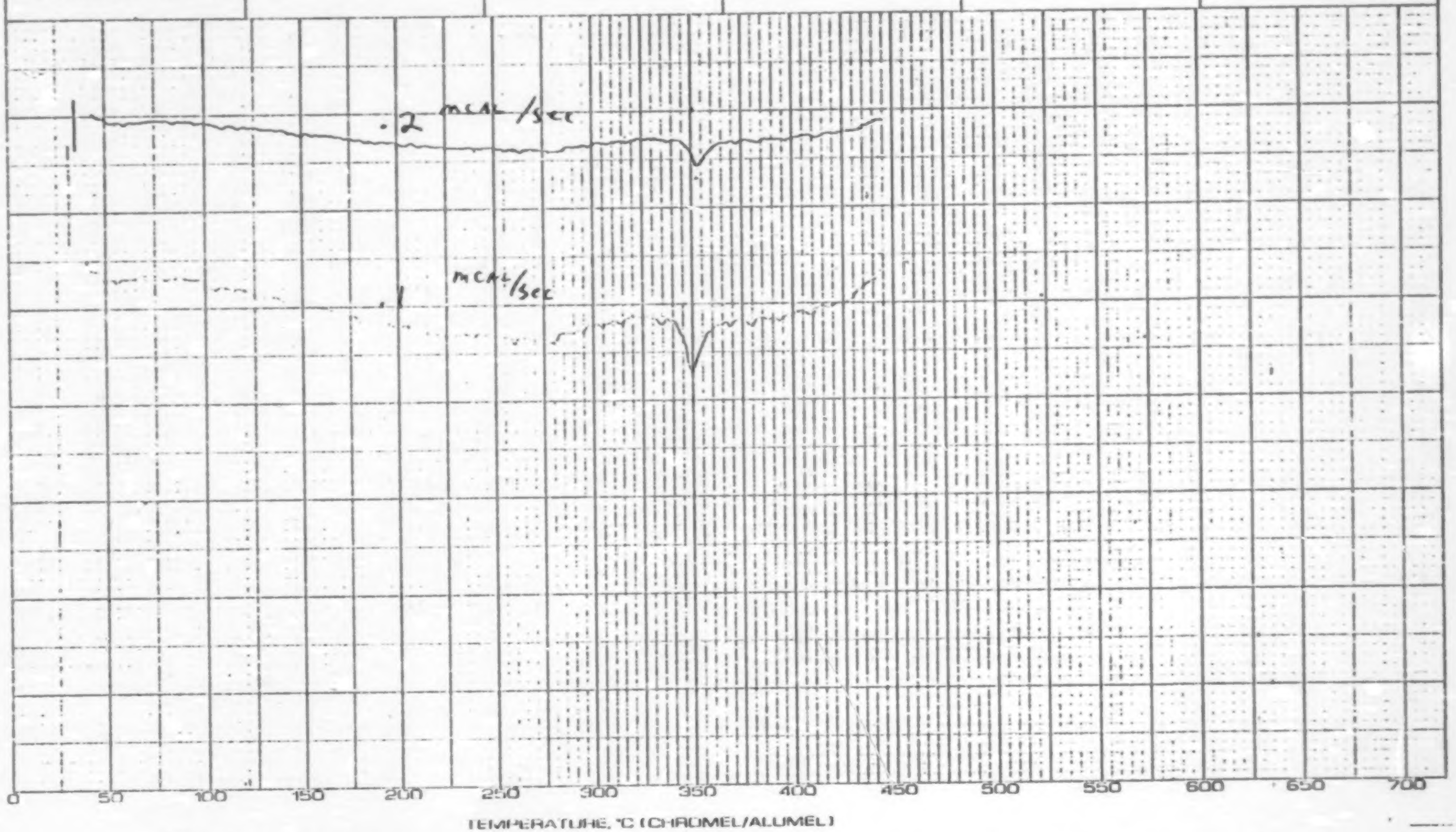
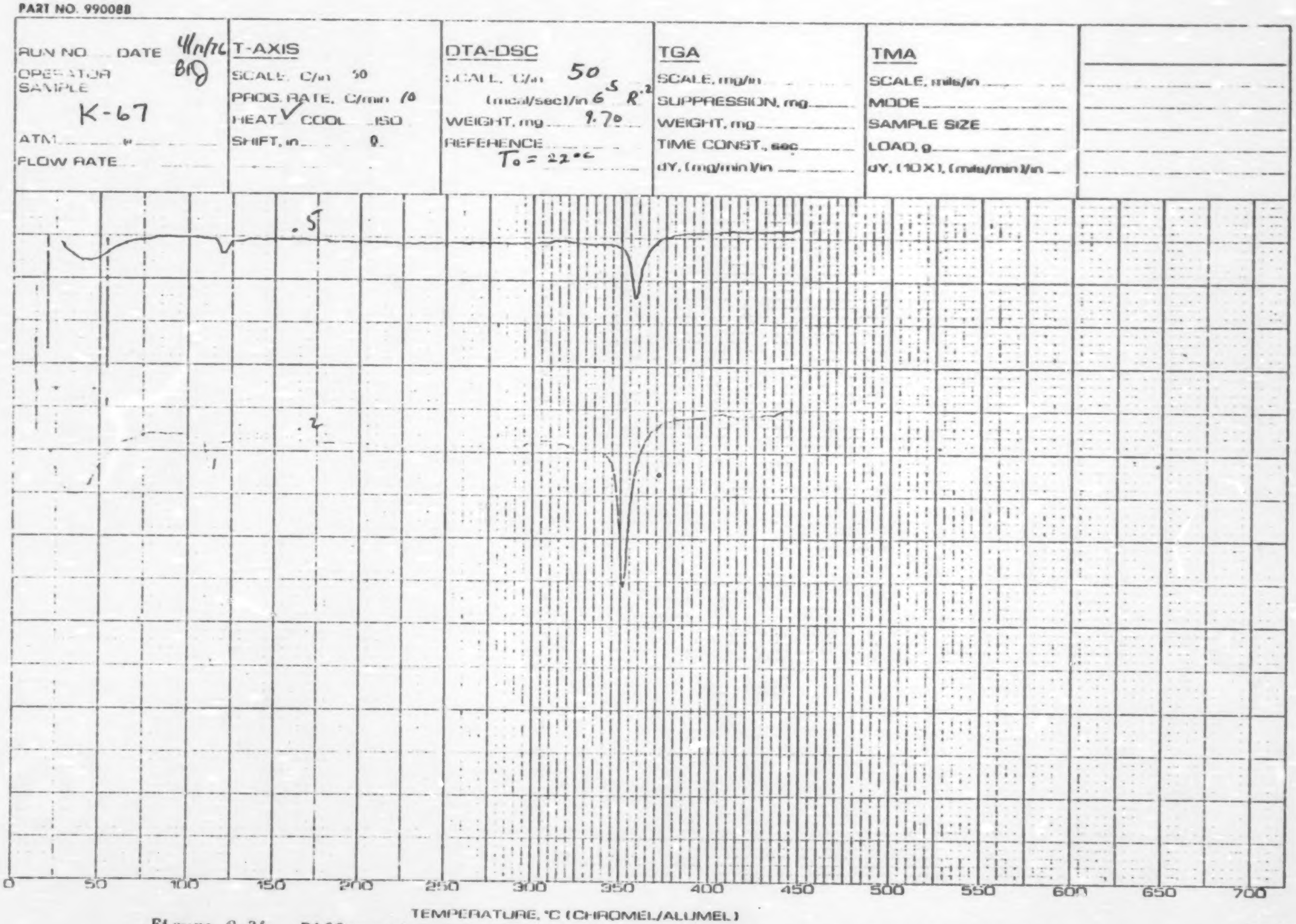


Figure G-33. Differential Calorimetry Scan of Solids Precipitated from Kinetic Run No. 66


PART NO. 990088

RUN NO. DATE 4/11/76
OPERATOR BRD
SAMPLE K-67
ATM
FLOW RATE

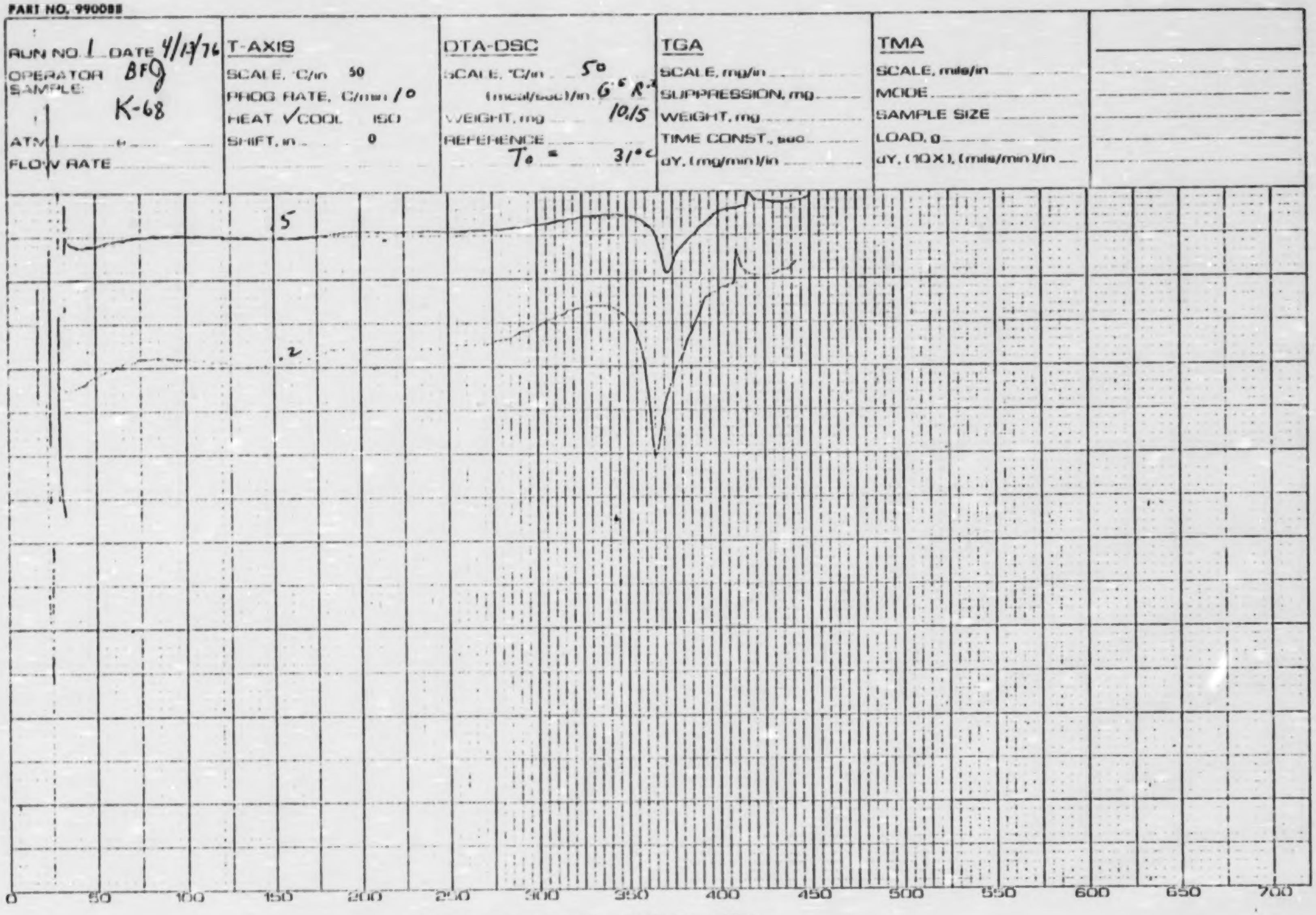
T-AXIS
SCALE, C/in 50
PROG. RATE, C/min 10
HEAT ✓ COOL ISO
SHIFT, in 0

DTA-DSC
SCALE, C/in 50
(mcal/sec)/in 6^{5} $R^{.2}$
WEIGHT, mg 9.70
REFERENCE
$T_0 = 22°C$

TGA
SCALE, mg/in
SUPPRESSION, mg
WEIGHT, mg
TIME CONST., sec
dY, (mg/min)/in

TMA
SCALE, mils/in
MODE
SAMPLE SIZE
LOAD, g
dY, (10X), (mils/min)/in

Figure G-34. Differential Calorimetry Scan of Solids Precipitated from Kinetic Run No. 67



PART NO. 990088

RUN NO. 1 DATE 4/13/76
OPERATOR BFG
SAMPLE: K-68
ATM
FLOW RATE

T-AXIS
SCALE, °C/in 50
PROG RATE, °C/min 10
HEAT ✓COOL 150
SHIFT, in 0

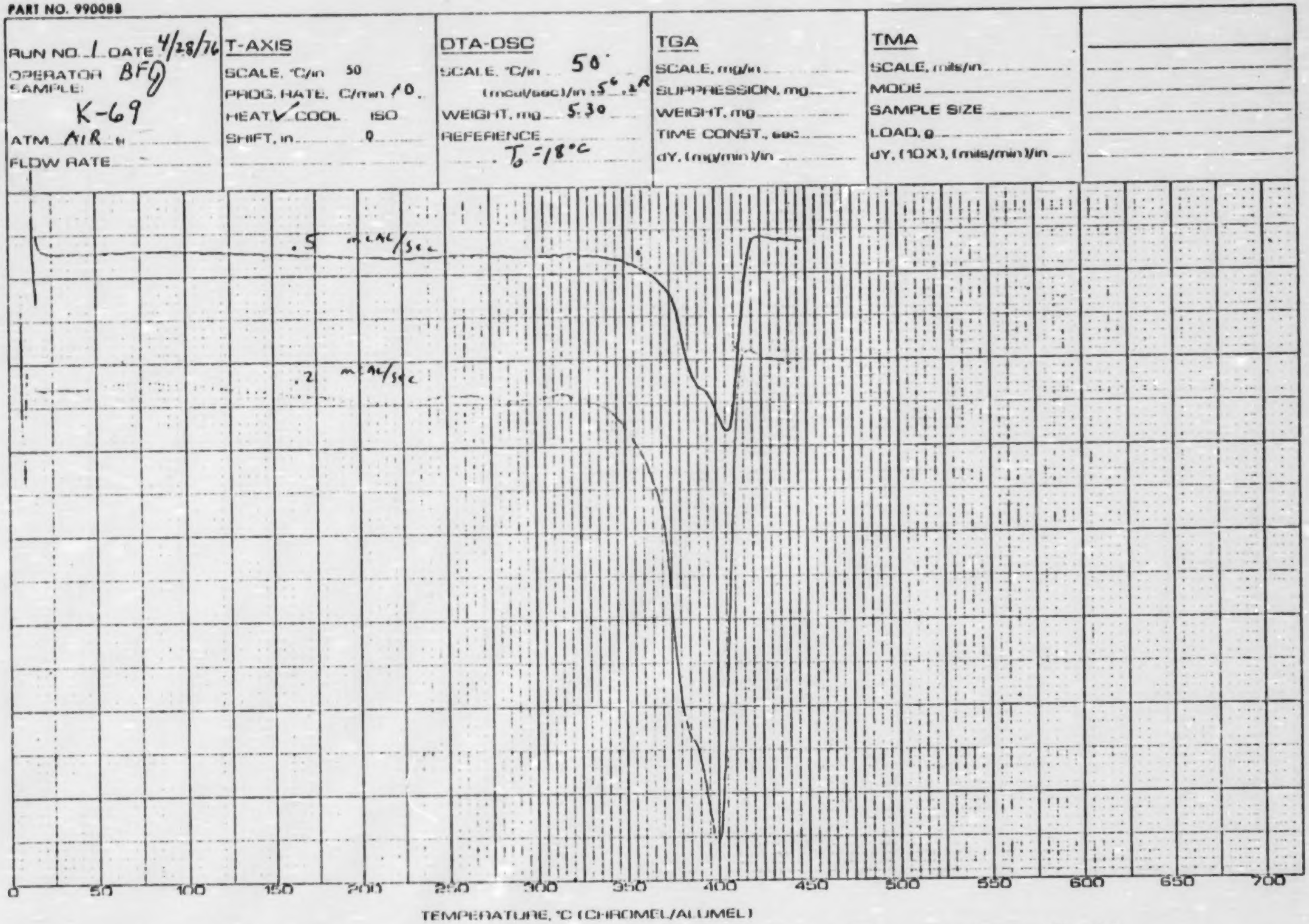
DTA-DSC
SCALE, °C/in 50
(mcal/sec)/in 6.6 R
WEIGHT, mg 10.15
REFERENCE
T_0 = 31°C

TGA
SCALE, mg/in
SUPPRESSION, mg
WEIGHT, mg
TIME CONST., sec
dY, (mg/min)/in

TMA
SCALE, mils/in
MODE
SAMPLE SIZE
LOAD, g
dY, (10X), (mils/min)/in

Figure G-35. Differential Calorimetry Scan of Solids Precipitated from Kinetic Run No. 68

PART NO. 990088



RUN NO. 1 DATE 4/28/76
OPERATOR BFG
SAMPLE: K-69
ATM AIR
FLOW RATE -

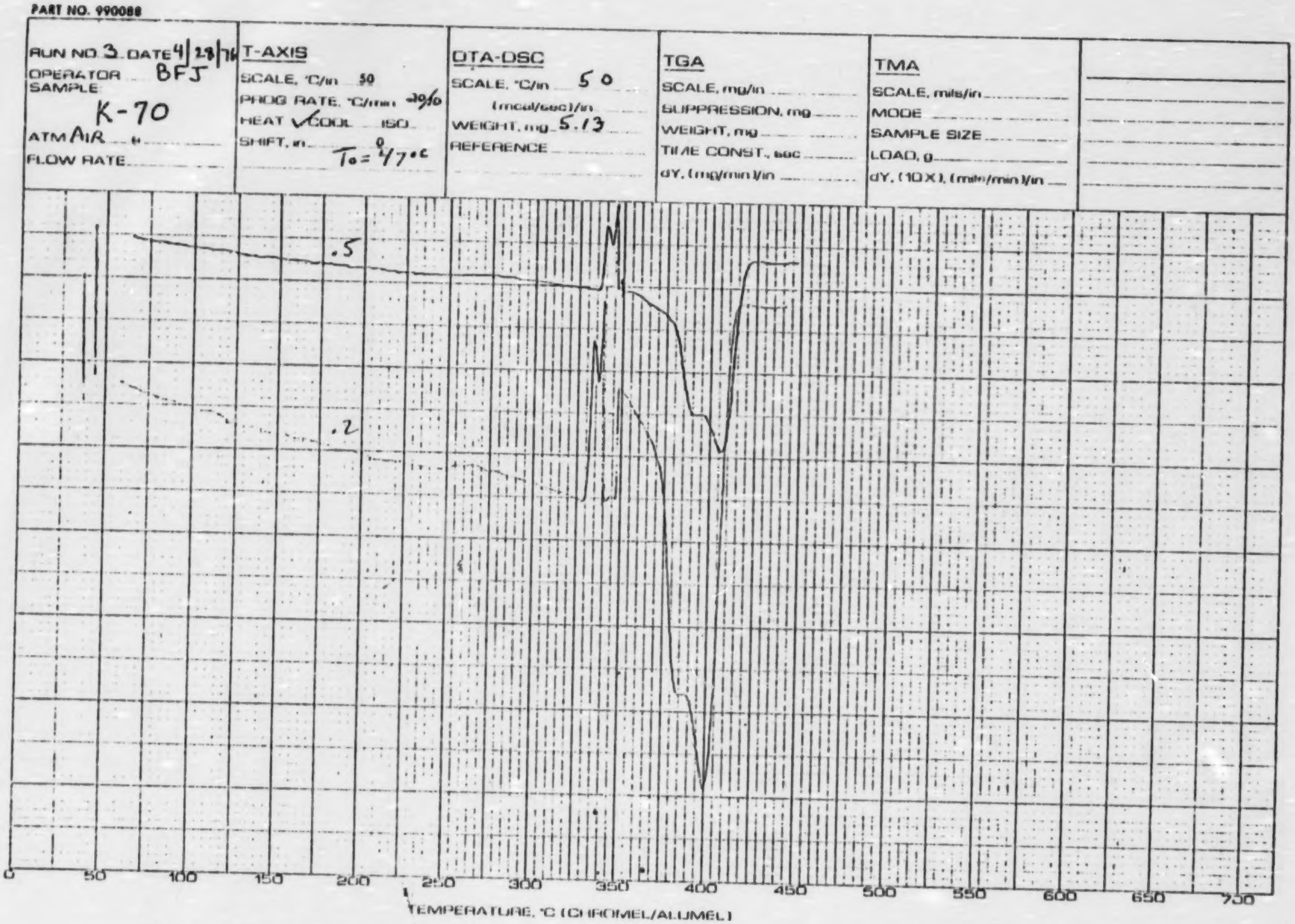
T-AXIS
SCALE, °C/in 50
PROG. RATE, C/min 10.
HEAT ✓ COOL ISO
SHIFT, in 0

DTA-DSC
SCALE, °C/in 50°
(mcal/sec)/in .5^S .2^R
WEIGHT, mg 5.30
REFERENCE
T_0 = 18°C

TGA
SCALE, mg/in
SUPPRESSION, mg
WEIGHT, mg
TIME CONST., sec
dY, (mg/min)/in

TMA
SCALE, mils/in
MODE
SAMPLE SIZE
LOAD, g
dY, (10X), (mils/min)/in

Figure C-36. Differential Calorimetry Scan of Solids Precipitated from Kinetic Run No. 69


PART NO. 990088

RUN NO 3 DATE 4/28/76
OPERATOR BFJ
SAMPLE K-70
ATM AIR
FLOW RATE

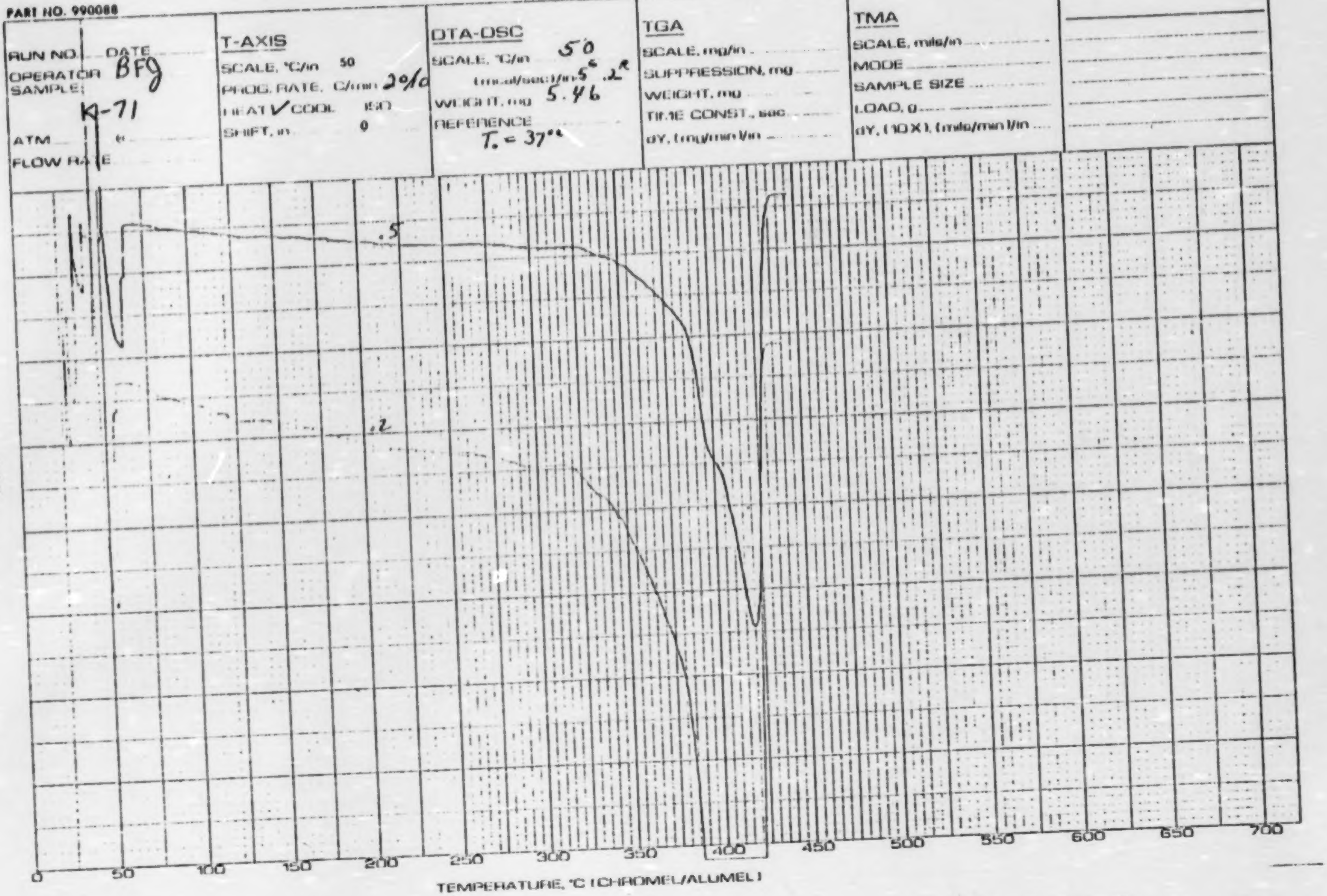
T-AXIS
SCALE, °C/in 50
PROG RATE, °C/min 20/10
HEAT ✓COOL ISO
SHIFT, in 0 $T_0 = 47°C$

DTA-DSC
SCALE, °C/in 5 0
(mcal/sec)/in
WEIGHT, mg 5.13
REFERENCE

TGA
SCALE, mg/in
SUPPRESSION, mg
WEIGHT, mg
TIME CONST., sec
dY, (mg/min)/in

TMA
SCALE, mils/in
MODE
SAMPLE SIZE
LOAD, g
dY, (10X), (mils/min)/in

Figure C-37. Differential Calorimetry Scan of Solids Precipitated from Kinetic Run No. 70



PART NO. 990088

RUN NO. ___ DATE ___
OPERATOR BFG
SAMPLE: K-71
ATM ___
FLOW RATE ___

T-AXIS
SCALE, °C/in 50
PROG. RATE, C/min 20/d
HEAT ✓ COOL 150
SHIFT, in 0

DTA-DSC
SCALE, °C/in 50
(mcal/sec)/in 5 .2
WEIGHT, mg 5.46
REFERENCE
$T_0 = 37°$

TGA
SCALE, mg/in ___
SUPPRESSION, mg ___
WEIGHT, mg ___
TIME CONST., sec ___
dY, (mg/min)/in ___

TMA
SCALE, mils/in ___
MODE ___
SAMPLE SIZE ___
LOAD, g ___
dY, (10X), (mils/min)/in ___

Figure G-38. Differential Calorimetry Scan of Solids Precipitated from Kinetic Run No. 71

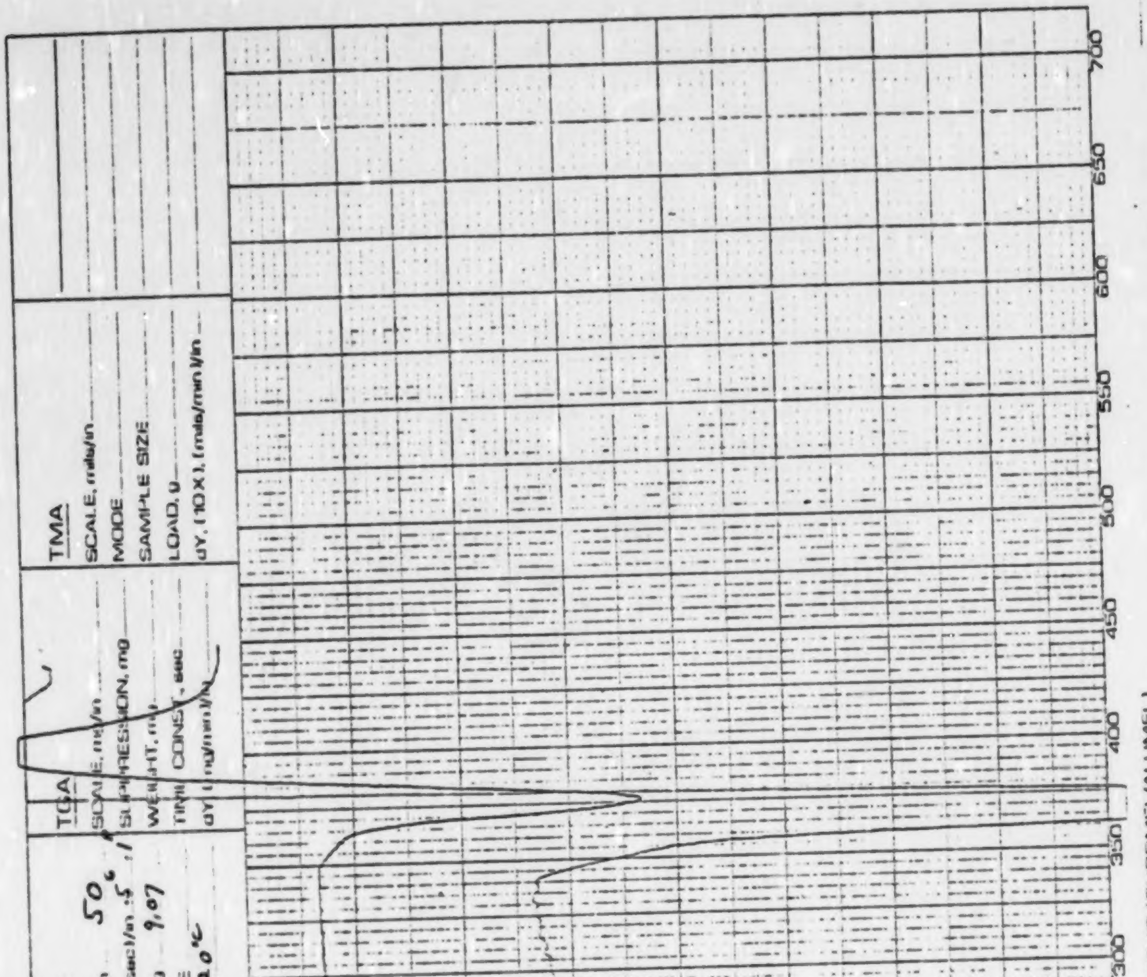
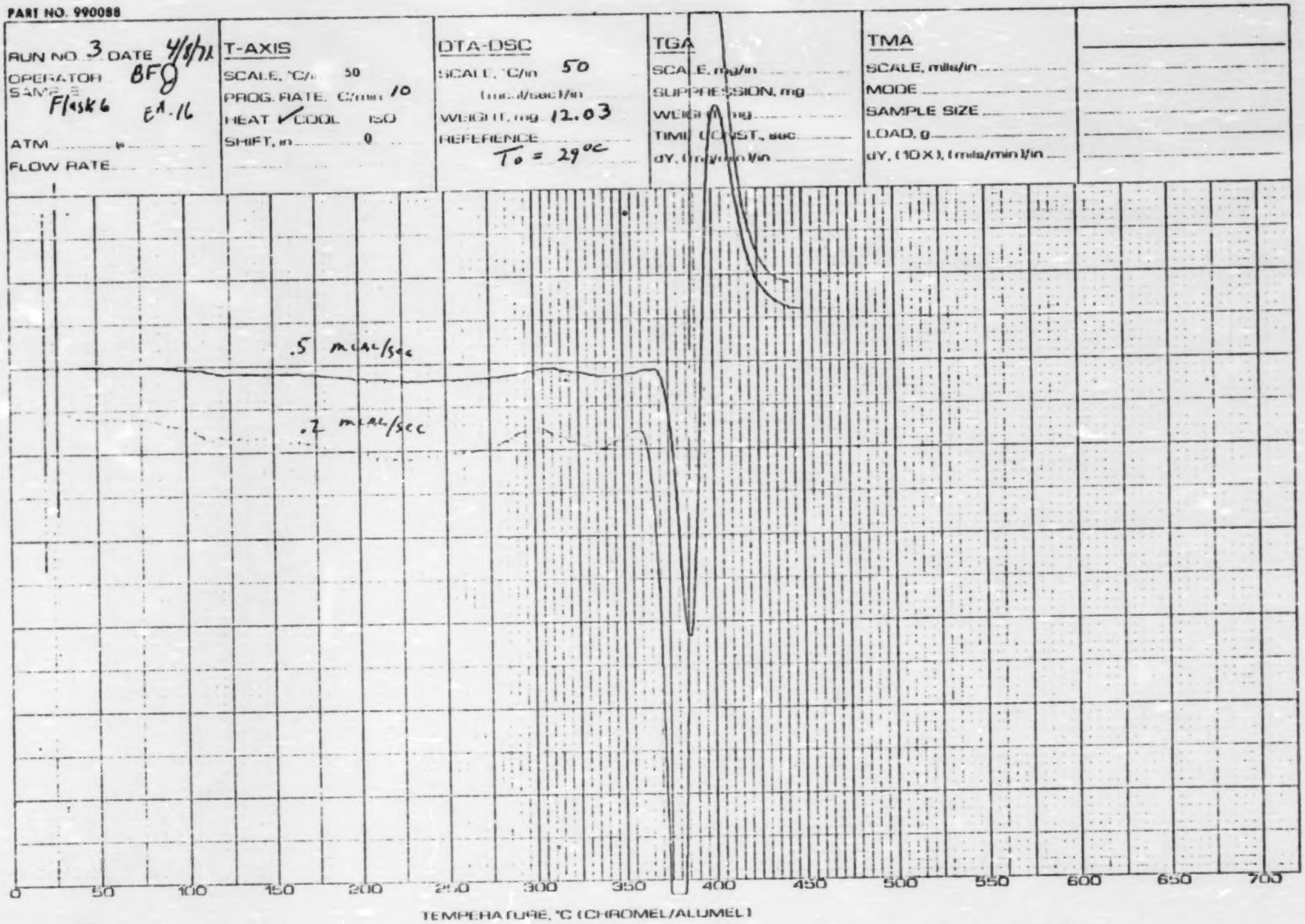


Figure G-39. Differential Calorimetry Scan of Solids Precipitated from Equilibrium Run E*-15



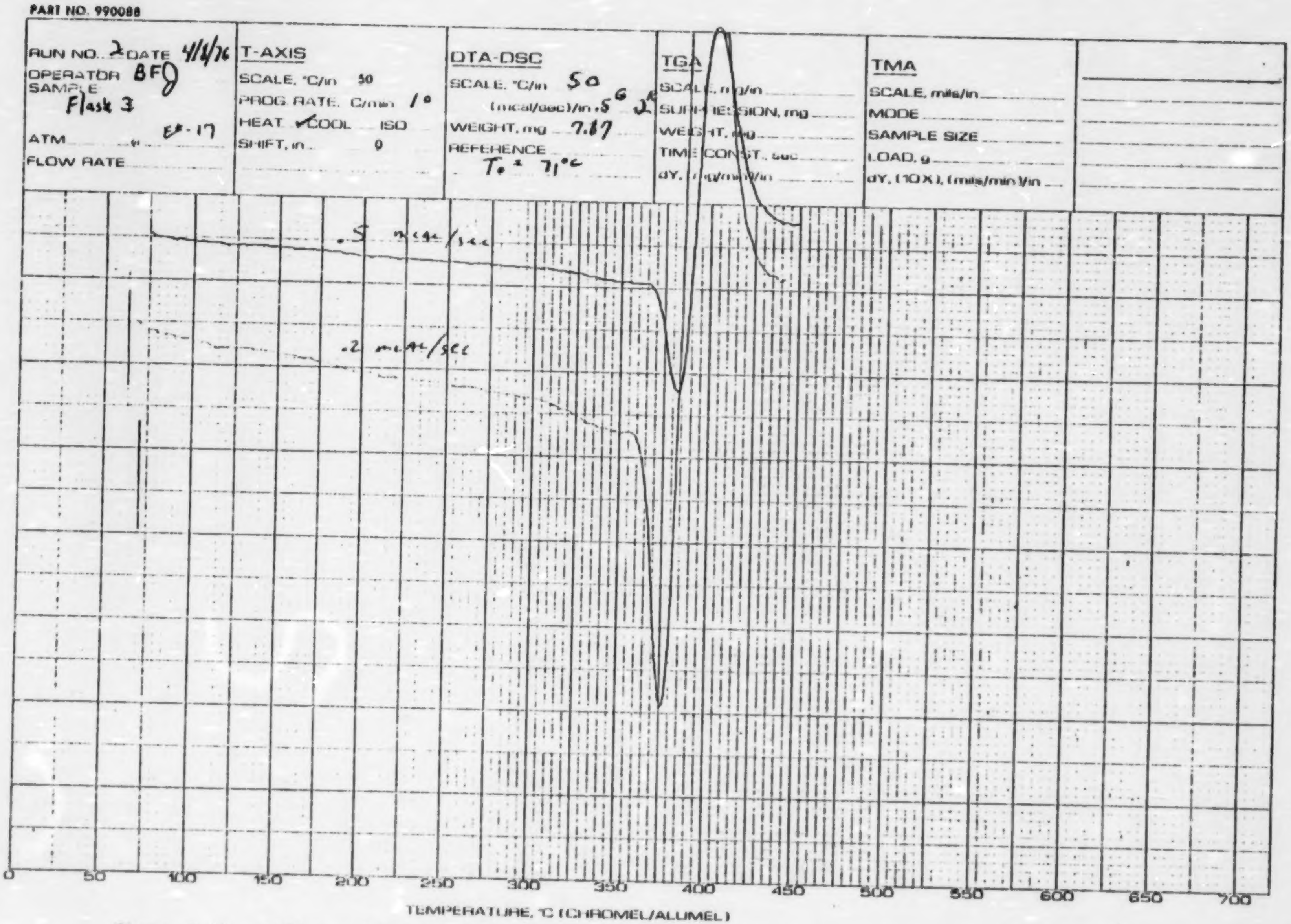
PART NO. 990088

RUN NO. 3 DATE 4/8/71
OPERATOR BFG
SAMPLE Flask 6 E*-16
ATM
FLOW RATE

T-AXIS
SCALE, °C/in 50
PROG. RATE, C/min 10
HEAT ✓ COOL ISO
SHIFT, in 0

DTA-DSC
SCALE, °C/in 50
(mcal/sec)/in
WEIGHT, mg 12.03
REFERENCE
$T_0 = 29°C$

Figure C-40. Differential Calorimetry Scan of Solids Precipitated from Equilibrium Run E*-16



PART NO. 990088

RUN NO. 2 DATE 4/8/76
OPERATOR BFG
SAMPLE
Flask 3
E*-17
ATM
FLOW RATE

T-AXIS
SCALE, °C/in 50
PROG. RATE, C/min 10
HEAT ✓COOL ISO
SHIFT, in 0

DTA-DSC
SCALE, °C/in 50
(mcal/sec)/in .5 .2
WEIGHT, mg 7.87
REFERENCE
T_0 = 71°C

TGA
SCALE, mg/in
SUPPRESSION, mg
WEIGHT, mg
TIME CONST., sec
dY, (mg/min)/in

TMA
SCALE, mils/in
MODE
SAMPLE SIZE
LOAD, g
dY, (10X), (mils/min)/in

Figure G-41. Differential Calorimetry Scan of Solids Precipitated from Equilibrium Run E*-17

PART NO. 990088

RUN NO 2 DATE 3-22-76
OPERATOR QQ8
SAMPLE HTS 1/19-23/76
ATM Covered pan
FLOW RATE

T-AXIS
SCALE, C/in 50
PROG RATE, C/min 10
HEAT ✓ COOL ISO
SHIFT, in 0

DTA-DSC
SCALE, °C/in ~~ ~~ 50
(mcal/sec)/in °
WEIGHT, mg 3.40
REFERENCE Empty pan

TGA
SCALE, mg/in
SUPPRESSION, mg
WEIGHT, mg
TIME CONST., sec
dY, (mg/min)/in

TMA
SCALE, mils/in mcal/g mcal
MODE 23°, 3.67 .0125
SAMPLE 24 SIZE .98 .0035
LOAD, g
dY, (10X), (mils/min)/in

.0031 5.10
.0035 4.51
709 220x10^-6

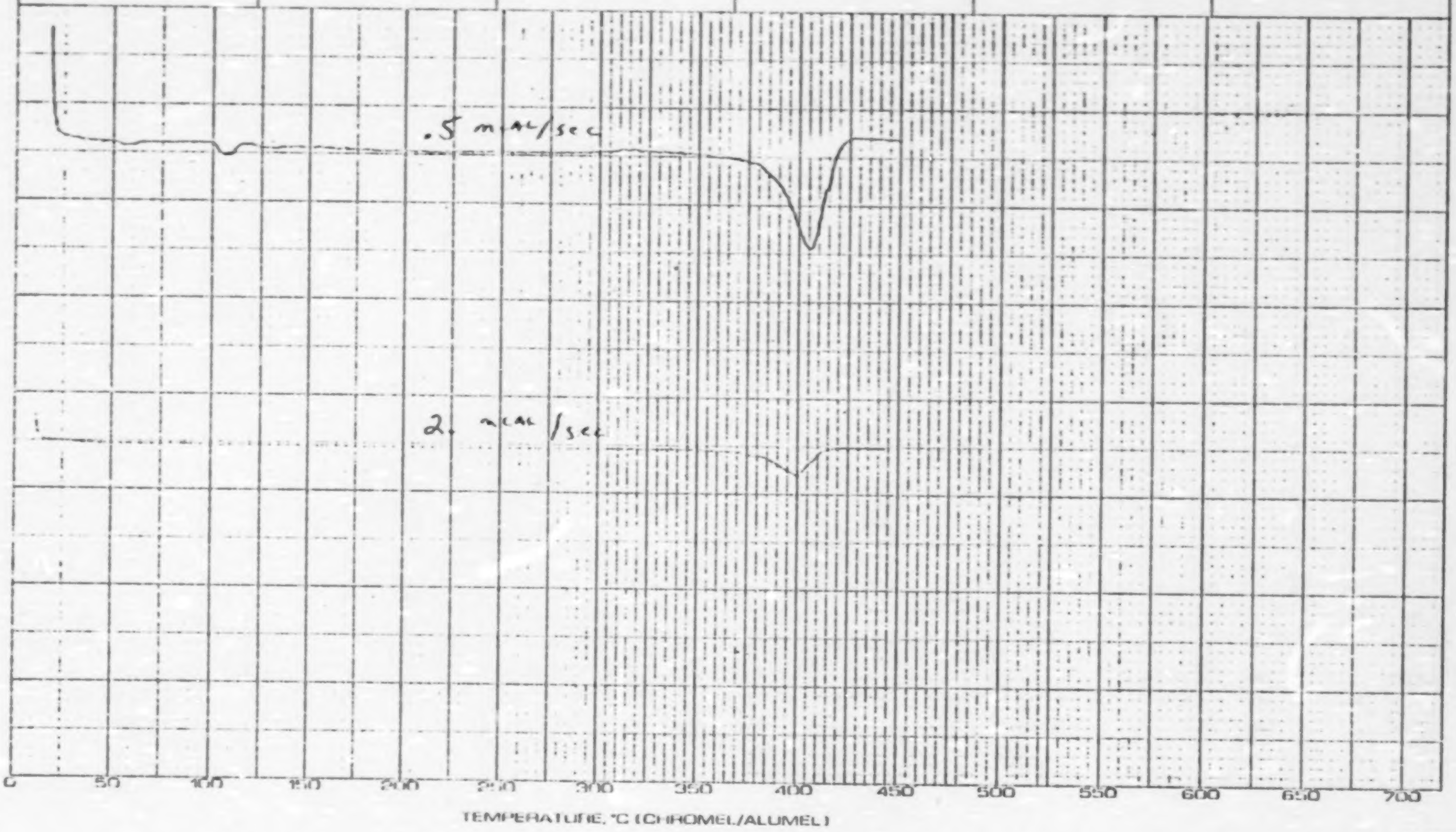
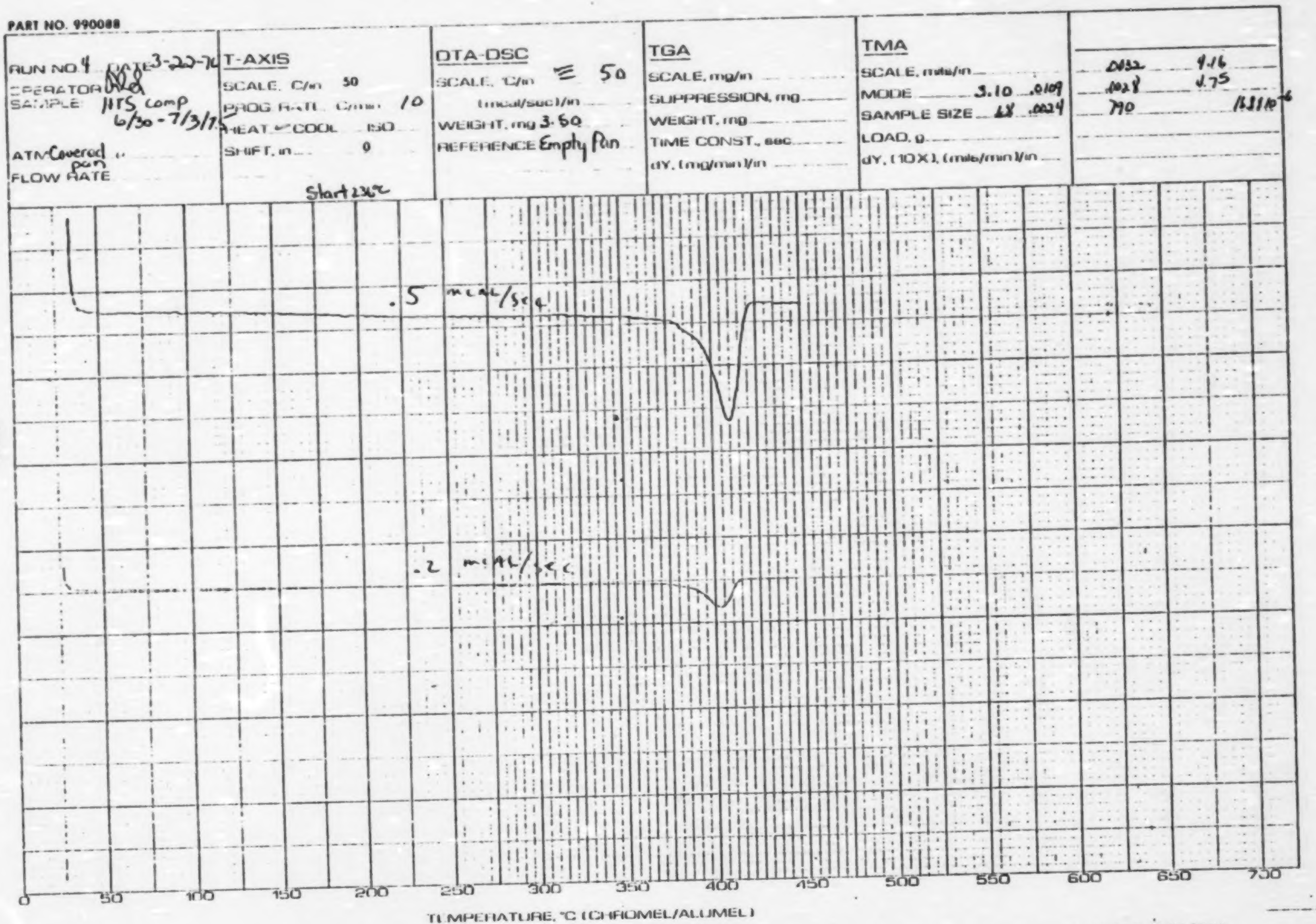


Figure G-42. Differential Calorimetry Scans of EPA/RTP Holding Tank Solids Precipitated (1/19-23/76)



PART NO. 990088

RUN NO. 4 DATE 3-22-76
OPERATOR
SAMPLE: HTS comp 6/30-7/3/75
ATM Covered pan
FLOW RATE

T-AXIS
SCALE, C/in 50
PROG RATE, C/min 10
HEAT / COOL 150
SHIFT, in 0
Start 236°c

DTA-DSC
SCALE, °C/in ≡ 50
(mcal/sec)/in
WEIGHT, mg 3.50
REFERENCE Empty Pan

TGA
SCALE, mg/in
SUPPRESSION, mg
WEIGHT, mg
TIME CONST., sec
dY, (mg/min)/in

TMA
SCALE, mils/in
MODE 3.10 .0109
SAMPLE SIZE 68 .0024
LOAD, g
dY, (10X), (mils/min)/in

.0032 9.16
.0028 9.75
790 1.83×10^{-6}

.5 mcal/sec
.2 mcal/sec
0
50
100
150
200
250
300
350
400
450
500
550
600
650
700
TEMPERATURE, °C (CHROMEL/ALUMEL)

Figure C-43. Differential Calorimetry Scans of EPA/RTP Holding Tank Solids Precipitated (6/30-7/3/75)